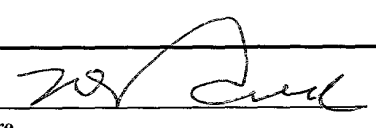


526 Rec'd PCT/PTO 13 JUL 2001

FORM PTO-1390 OFFICE (REV. 10-95)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK		ATTORNEY'S DOCKET NUMBER	
<b>TRANSMITTAL LETTER TO THE UNITED STATES          DESIGNATED/ELECTED OFFICE (DO/EO/US)          CONCERNING A FILING UNDER 35 U.S.C. 371</b>				<b>CM2006XM</b> U.S. APPLICATION NO. (if known, see 37 CFR 1.5) <b>09/889253</b>	
INTERNATIONAL APPLICATION NO. <b>PCT/US00/00838</b>		INTERNATIONAL FILING DATE <b>13 January 2000</b>		PRIORITY DATE CLAIMED <b>14 January 1999</b>	
TITLE OF INVENTION <b>Detergent Compositions Comprising A Pectate Lyase and A Bleach System</b>					
APPLICANT(S) FOR DO/EO/US <b>SHOWELL, Michael Stanford et al.</b>					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.					
1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371. 3. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(l). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application was filed (35 U.S.C. 371(c)(2)) a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> has been transmitted by the International Bureau. c. <input checked="" type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). Items 11. to 16. below concern document(s) or information included: 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment. 14. <input type="checkbox"/> A substitute specification. 15. <input checked="" type="checkbox"/> A change of power of attorney and/or address letter. 16. <input type="checkbox"/> Other items or information:					
"Express Mail" mailing label number <b>EL483620561745 650215 WEB</b> Date of Deposit <b>13 July 2001</b> I hereby certify that this paper/letters being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to The Assistant Commissioner of Patents, Washington, D.C. 20231 Administrator Mailing Application. Signature <i>Margaret Byrd</i>					

09889253 PCT/PTO

JC18 Rec'd PCT/PTO 13 JUL 2001

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) <b>09/889253</b>		INTERNATIONAL APPLICATION NO. PCT/US00/00838		ATTORNEY'S DOCKET NUMBER CM2006XM	
				CALCULATIONS PTO USE ONLY	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$710	
Surcharge of \$130.00 for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$0	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	30-20 =	10	x \$18.00	\$180	
Independent Claims	1-3 =	0	x \$80.00	\$0	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			\$270.00	\$0	
TOTAL OF ABOVE CALCULATIONS =				\$890	
Processing fee of \$130.00 for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$0	
TOTAL NATIONAL FEE =				\$890	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28,3.31). \$40.00 per property +				\$0	
TOTAL FEES ENCLOSED =				\$890	
				Amount to be refunded	\$
				charged	\$
<p>a. [ ] A check in the amount of \$ ____ to cover the above fees is enclosed.</p> <p>b. [ x ] Please charge my Deposit Account No. <u>16-2480</u> in the amount of \$ <u>890</u> to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. [ x ] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>16-2480</u>. A duplicate copy of this sheet is enclosed.</p> <p>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</p> <p>SEND ALL CORRESPONDENCE TO:</p>					
F. Taffy Customer Number 27748				 Signature T. David Reed Name 32,931 Registration Number	

09889253

Case CM2006XM

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the Matter of:

U.S. National Phase Entry

Under 35 USC § 371 from

the International Application of :

SHOWELL, Michael Stanford et al :

Int'l Application No. PCT/US00/00838 :

Filed in the RO/US on 13 January 2000 :

Entitled: DETERGENT COMPOSITIONS COMPRISING A  
PECTATE LYASE AND A BLEACH SYSTEM

PRELIMINARY AMENDMENT UNDER 37 CFR § 1.112

Assistant Commissioner for Patents

Washington, D.C. 20231

Dear Sir:

Prior to Examination and computation of the fees for entering the captioned International Application into the U.S. National Phase, please preliminarily amend the above-identified application as follows and consider the following Remarks.

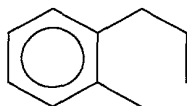
AMENDMENTSIN THE CLAIMS

Please amend Claims as follows:

2. A detergent composition according to claim 1 wherein the metal bleach catalyst is selected from :
  - (a) the [Mn(Bcyclam)Cl<sub>2</sub>] catalyst;
  - (b) the cobalt catalyst having the formula :  $\text{Co}[(\text{NH}_3)_n\text{M}_m\text{B}_b\text{T}_t\text{Q}_q\text{P}_p]\text{Y}_y$  wherein Cobalt is in the +3 oxidation from, n is an integer from 0 to 5; M represents a monodentate ligand; m is an integer from 0-5; B represents a bidentate ligand; b is an integer from 0-2; T represents a tridentate ligand; t is 0 or 1; Q is a tetradentate ligand; q is 0 or 1; P is an pentadentate ligand; p is 0 or 1 and  $n+m+2b+3t+4q+5p=6$ ; Y is one or more appropriately selected counteranions present in a number y, where y is an integer from 1-3 when Y is a -1 charged anion, to obtain a charge-balanced salt;
  - (c) the cobalt catalyst having the formula  $[\text{Co}(\text{NH}_3)_5\text{M}]\text{T}_y$  wherein cobalt is in the +3 oxidation state; M is a carboxylate-containing ligand having the formula

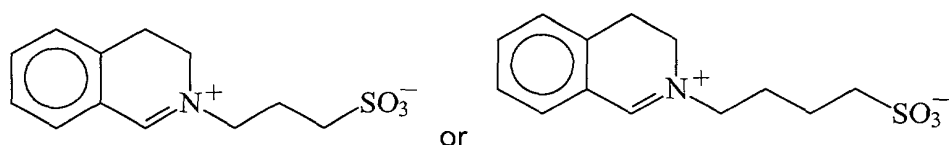
RC(O)O<sup>-</sup>; and T is one or more counteranions present in a number y, where y is an interger to obtain a charge-balanced salt; and/or mixtures thereof.

3. A detergent composition according to claim 2 comprising said metal bleach catalyst and further comprising a peroxygen source.
4. A composition according to claim 3 wherein the metal bleach catalyst is present in an amount of from 1ppb to 10% by weight of total composition.
5. A detergent composition according to claim 1 wherein said diacyl peroxide is selected from the group consisting of dibenzoyl peroxide, benzoyl glutaryl peroxide, benzoyl succinyl peroxide, di(2-methyl benzoyl) peroxide, and/or mixtures thereof.
7. A detergent composition according to claim 1 wherein said diacyl peroxide is comprised in a particle; said particle comprising from 1-80% by weight of said particle of diacyl peroxide, from 0.01-95% by weight of said particle of a water soluble stabilising additive.
9. A detergent composition according to claim 4 wherein said diacyl peroxide is dilauroyl peroxide.
10. A detergent composition according to claim 1 wherein said diacyl peroxide is comprised at a level of from 0.01% to 20% by weight of the composition.
11. A detergent composition according to claim 10 wherein the diacyl peroxide is incorporated into a particulate and said particle is comprised at a level of from 0.1% to 30% of the total composition.
12. A detergent composition according to claim 1 wherein said bleach booster is selected from the group consisting of aryliminium zwitterions, aryliminium polyions having a net negative charge of from -1 to -3; and/or mixtures thereof.
14. A detergent composition according to claim 13 wherein R<sup>1</sup> and R<sup>2</sup> together form the non-charged moiety:

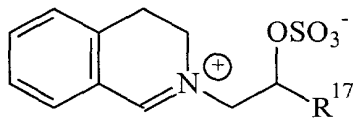




15. A detergent composition according to claim 14 wherein said bleach booster is an aryliminium zwitterion and  $R^3$  is H, T is  $-(CH_2)_b-$  or  $-CH_2(C_6H_4)-$ , Z is  $-SO_3^-$ , a is 1 and b is from 2 to 4.
16. A detergent composition according to claim 15 wherein said bleach booster is an aryliminium zwitterion having the formula:



19. A detergent composition according to claim 18 wherein said bleach booster is an aryliminium zwitterion and  $R^3$  is H, Z is  $-OSO_3^-$ , a is 1.
20. A detergent composition according to claim 19 wherein said bleach booster is an aryliminium zwitterion having the formula:



where  $R^{17}$  is selected from the group consisting of H and linear or branched  $C_1$ - $C_{18}$  substituted or unsubstituted alkyl.

21. A detergent composition according to claim 1 wherein said bleach booster is comprised at a level of from 0.01% to 10% by weight of the total composition.
22. A detergent composition according to claim 21 wherein said peroxygen source is comprised at a level of from 0.01% to 60% by weight of the total composition.
23. A detergent composition according to claim 22 wherein said peroxygen source comprises a preformed peracid compound selected from the group consisting of percarboxylic acids and salts, percarbonic acids and salts, perimidic acids and salts, peroxymonosulfuric acids and salts, and/or mixtures thereof; a hydrogen peroxide source, a bleach activator and/or mixtures thereof.

26. A detergent composition according to claim 1 wherein said pectate lyase is present at a level of from 0.0001% to 2% pure enzyme by weight of total composition.
27. A detergent composition according to claim 1 further comprising a pectin lyase.
28. Use of a composition according to claim 1 for the removal of plant-, dirt-based stains, highly coloured food soils/stains and body soils.
29. Use of a composition according to claim 1 for superior fabric whiteness maintenance.
30. Use of a composition according to claim 11 for effective highly coloured stains and soils removal on plasticware, and/or for preventing the staining and/or discolouration of the dishware by highly coloured components.

Year	Total population		Male		Female		Total population	Male		Female		Total population	Male		Female			
	Population	%	Population	%	Population	%		Population	%	Population	%		Population	%	Population	%		
1950	1,000,000	100	500,000	50	500,000	50	1,000,000	100	500,000	50	500,000	50	1,000,000	100	500,000	50	500,000	50
1955	1,050,000	105	525,000	50	525,000	50	1,050,000	105	525,000	50	525,000	50	1,050,000	105	525,000	50	525,000	50
1960	1,100,000	110	550,000	50	550,000	50	1,100,000	110	550,000	50	550,000	50	1,100,000	110	550,000	50	550,000	50
1965	1,150,000	115	575,000	50	575,000	50	1,150,000	115	575,000	50	575,000	50	1,150,000	115	575,000	50	575,000	50
1970	1,200,000	120	600,000	50	600,000	50	1,200,000	120	600,000	50	600,000	50	1,200,000	120	600,000	50	600,000	50
1975	1,250,000	125	625,000	50	625,000	50	1,250,000	125	625,000	50	625,000	50	1,250,000	125	625,000	50	625,000	50
1980	1,300,000	130	650,000	50	650,000	50	1,300,000	130	650,000	50	650,000	50	1,300,000	130	650,000	50	650,000	50
1985	1,350,000	135	675,000	50	675,000	50	1,350,000	135	675,000	50	675,000	50	1,350,000	135	675,000	50	675,000	50
1990	1,400,000	140	700,000	50	700,000	50	1,400,000	140	700,000	50	700,000	50	1,400,000	140	700,000	50	700,000	50
1995	1,450,000	145	725,000	50	725,000	50	1,450,000	145	725,000	50	725,000	50	1,450,000	145	725,000	50	725,000	50
2000	1,500,000	150	750,000	50	750,000	50	1,500,000	150	750,000	50	750,000	50	1,500,000	150	750,000	50	750,000	50
2005	1,550,000	155	775,000	50	775,000	50	1,550,000	155	775,000	50	775,000	50	1,550,000	155	775,000	50	775,000	50
2010	1,600,000	160	800,000	50	800,000	50	1,600,000	160	800,000	50	800,000	50	1,600,000	160	800,000	50	800,000	50
2015	1,650,000	165	825,000	50	825,000	50	1,650,000	165	825,000	50	825,000	50	1,650,000	165	825,000	50	825,000	50
2020	1,700,000	170	850,000	50	850,000	50	1,700,000	170	850,000	50	850,000	50	1,700,000	170	850,000	50	850,000	50
2025	1,750,000	175	875,000	50	875,000	50	1,750,000	175	875,000	50	875,000	50	1,750,000	175	875,000	50	875,000	50
2030	1,800,000	180	900,000	50	900,000	50	1,800,000	180	900,000	50	900,000	50	1,800,000	180	900,000	50	900,000	50
2035	1,850,000	185	925,000	50	925,000	50	1,850,000	185	925,000	50	925,000	50	1,850,000	185	925,000	50	925,000	50

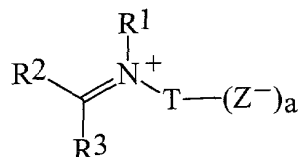
13 July 2001  
5299 Spring Grove Avenue  
Cincinnati, Ohio 45217-1087  
Phone: (513) 627-7025  
FAX: (513) 627-6333

VERSION WITH MARKINGS TO SHOW CHANGES MADE

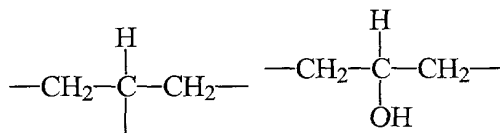
In the claims:

1. A detergent composition comprising a detergent ingredient, a pectate lyase enzyme and bleach system selected from the group consisting of a metal bleach catalyst; a combination of a peroxygen source and a bleach booster selected from the group consisting of zwitterionic imines, anionic imine polyions having a net negative charge of from -1 to -3, and/or mixtures thereof; a diacyl peroxide and/or mixtures thereof.
2. A detergent composition according to claim 1 wherein the metal bleach catalyst is selected from :
  - (a) the  $[Mn(Bcyclam)Cl_2]$  catalyst;
  - (b) the cobalt catalyst having the formula :  $Co[(NH_3)_n M_m B_b T_t Q_q P_p] Y_y$  wherein Cobalt is in the +3 oxidation from, n is an integer from 0 to 5[, preferably 4-5, more preferably 5]; M represents a monodentate ligand; m is an integer from 0-5[, preferably 1 or 2, more preferably 1]; B represents a bidentate ligand; b is an integer from 0-2; T represents a tridentate ligand; t is 0 or 1; Q is a tetradentate ligand; q is 0 or 1; P is an pentadentate ligand; p is 0 or 1 and  $n+m+2b+3t+4q+5p=6$ ; Y is one or more appropriately selected counteranions present in a number y, where y is an integer from 1-3[, preferably 2-3, more preferably 2] when Y is a -1 charged anion, to obtain a charge-balanced salt;
  - (c) the cobalt catalyst having the formula  $[Co(NH_3)_5 M] T_y$  wherein cobalt is in the +3 oxidation state; M is a carboxylate-containing ligand having the formula  $RC(O)O^-$ ; and T is one or more counteranions present in a number y, where y is an integer to obtain a charge-balanced salt [(preferably from 1-3, more preferably 2 when T is a -1 charged anion)]; and/or mixtures thereof.
3. A detergent composition according to claim 2 [1-2] comprising said metal bleach catalyst and further comprising a peroxygen source[, preferably selected from the group consisting of a hydrogen peroxide source, a peroxyacid bleach precursor compound, and/or mixtures thereof].
4. A composition according to claim 3 [claims 2-3] wherein the metal bleach catalyst is present in an amount of from 1ppb to 10%[, preferably from 0.1ppm to 1%, more preferably from 1ppm to 0.1%] by weight of total composition.

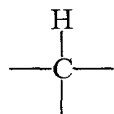
5. A detergent composition according to claim 1 [any of the preceding claims] wherein said diacyl peroxide is selected from the group consisting of dibenzoyl peroxide, benzoyl glutaryl peroxide, benzoyl succinyl peroxide, di(2-methyl benzoyl) peroxide, and/or mixtures thereof.
6. A detergent composition according to claim 5 wherein said diacyl peroxide is dibenzoyl peroxide.
7. A detergent composition according to claim 1 [any of the preceding claims] wherein said diacyl peroxide is comprised in a particle; said particle comprising from 1-80% by weight of said particle of diacyl peroxide, from 0.01-95% by weight of said particle of a water soluble stabilising additive.
8. A detergent composition according to claim 7 wherein said stabilising additive is selected from the group consisting of alkali metal sulfates and citrates, ethoxylated C16-20 alcohols, polyethylene glycols melting above 100°F, maltodextrins, polyacrylate polymers and copolymers of molecular weight between 1.000 and 80.000, ethylene diamine tetra-acetates, ethylene diamine disuccinates and/or mixtures thereof.
9. A detergent composition according to claim 4 [claim 1-4] wherein said diacyl peroxide is dilauroyl peroxide.
10. A detergent composition according to claim 1 [any of the preceding claims] wherein said diacyl peroxide is comprised at a level of from 0.01% to 20% by weight of the composition[, preferably 0.5% to 10%, more preferably 0.2% to 3%].
11. A detergent composition according to claim 10 [claims 7-10] wherein the diacyl peroxide is incorporated into a particulate and said particle is comprised at a level of from 0.1% to 30%[, preferably from 1% to 15%, more preferably from 1.5% to 10%] of the total composition.
12. A detergent composition according to claim 1 [any of the preceding claims] wherein said bleach booster is selected from the group consisting of aryliminium zwitterions, aryliminium polyions having a net negative charge of from -1 to -3; and/or mixtures thereof.
13. A detergent composition according to claim 12 wherein said bleach booster has the formula:



wherein  $\text{R}^1$ - $\text{R}^3$  are moieties having a total charge of from about 0 to about -1;  $\text{R}^1$  and  $\text{R}^2$  form part of a common ring; T is selected from the group consisting of:  $-(\text{CH}_2)_b-$  wherein b is from about 1 to about 8,  $-(\text{CH}(\text{R}^5))-$  wherein  $\text{R}^5$  is  $\text{C}_1$ - $\text{C}_8$  alkyl,  $-\text{CH}_2(\text{C}_6\text{H}_4)-$ ,

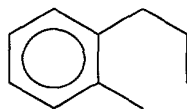


and  $-(\text{CH}_2)_d(\text{E})(\text{CH}_2)_f-$  wherein d is from 2 to 8, f is from 1 to 3 and E is  $-\text{C}(\text{O})\text{O}-$ ,  $-\text{C}(\text{O})\text{NR}^6$  or :

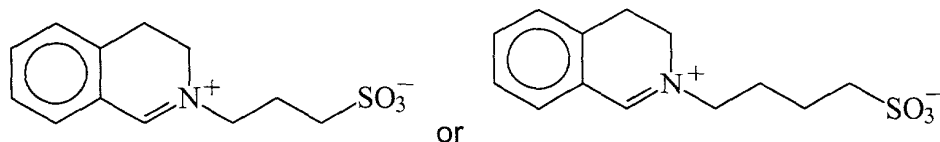


- wherein  $\text{R}^6$  is H or  $\text{C}_1$ - $\text{C}_4$  alkyl; Z is covalently bonded to T and Z is selected from the group consisting of  $-\text{CO}_2^-$ ,  $-\text{SO}_3^-$  and  $-\text{OSO}_3^-$  and a is either 1 or 2.

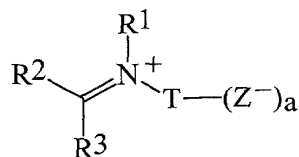
14. A detergent composition according to claim 13 [claims 12-13] wherein  $\text{R}^1$  and  $\text{R}^2$  together form the non-charged moiety:



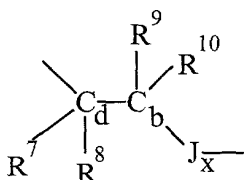
15. A detergent composition according to claim 14 [claims 12-14] wherein said bleach booster is an aryliminium zwitterion and  $\text{R}^3$  is H, T is  $-(\text{CH}_2)_b-$  or  $-\text{CH}_2(\text{C}_6\text{H}_4)-$ , Z is  $-\text{SO}_3^-$ , a is 1 and b is from 2 to 4.
16. A detergent composition according to claim 15 [claims 12-15] wherein said bleach booster is an aryliminium zwitterion having the formula:



17. A detergent composition according to claim 12 wherein said bleach booster bleach booster has the following formula:

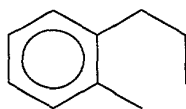


wherein  $R^1 - R^3$  is hydrogen or an unsubstituted or substituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl and cycloalkyl radicals;  $R^1$  and  $R^2$  form part of a common ring; T has the formula:



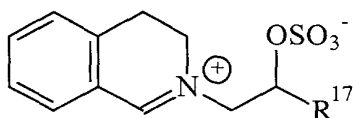
wherein  $x$  is equal to 0 or 1; J, when present, is selected from the group consisting of  $-CR^{11}R^{12}$ -,  $-CR^{11}R^{12}CR^{13}R^{14}$ -, and  $-CR^{11}R^{12}CR^{13}R^{14}CR^{15}R^{16}$ -;  $R^7$ - $R^{16}$  are selected from the group consisting of H, linear or branched  $C_1$ - $C_{18}$  substituted or unsubstituted alkyl, alkylene, oxyalkylene, aryl, substituted aryl, substituted arylcarbonyl groups, and amide groups; provided that at least one of  $R^7$ - $R^8$  must be H or methyl, and that when neither  $R^9$  nor  $R^{10}$  is H, one of  $R^7$ - $R^8$  must be H; Z is covalently bonded to  $J_x$  when  $x$  is 1 and to  $C_b$  when  $x$  is 0; and Z is selected from the group consisting of  $-CO_2^-$ ,  $-SO_3^-$  and  $-OSO_3^-$ , and  $a$  is 1.

18. A detergent composition according to claim 17 wherein said bleach booster wherein  $R^1$  and  $R^2$  are defined in its formula as  $R^1$  and  $R^2$  together form the non-charged moiety:



19. A detergent composition according to claim 18 [claims 17-18] wherein said bleach booster is an aryliminium zwitterion and  $R^3$  is H, Z is  $-OSO_3^-$ ,  $a$  is 1.

20. A detergent composition according to claim 19 [claims 17-19] wherein said bleach booster is an aryliminium zwitterion having the formula:



where R<sup>17</sup> is selected from the group consisting of H and linear or branched C<sub>1</sub>-C<sub>18</sub> substituted or unsubstituted alkyl.

21. A detergent composition according to claim 1 [any of the preceding claims] wherein said bleach booster is comprised at a level of from 0.01% to 10% by weight of the total composition.
22. A detergent composition according to claim 21 [claims 12-21] wherein said peroxygen source is comprised at a level of from 0.01% to 60% by weight of the total composition.
23. A detergent composition according to claim 22 [claims 12-22] wherein said peroxygen source comprises a preformed peracid compound selected from the group consisting of percarboxylic acids and salts, percarbonic acids and salts, perimidic acids and salts, peroxymonosulfuric acids and salts, and/or mixtures thereof; a hydrogen peroxide source, a bleach activator and/or mixtures thereof.
24. A detergent composition according to claim 23 wherein said hydrogen peroxide source is selected from the group consisting of perborate compounds, percarbonate compounds, perphosphate compounds and/or mixtures thereof.
25. A detergent composition according to claim 23 wherein said bleach activator is selected from the group consisting of tetraacetylenediamine, sodium decanoyloxybenzene sulfonate, sodium nonanoyloxybenzene sulfonate, sodium octanoyloxybenzene sulfonate, (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamido-caproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and/or mixtures thereof.
26. A detergent composition according to claim 1 [any of the preceding claims] wherein said pectate lyase is present at a level of from 0.0001% to 2%[, preferably from 0.0005% to 1.0, more preferably from 0.001% to 0.5%] pure enzyme by weight of total composition.



27. A detergent composition according to claim 1 [any of the preceding claims] further comprising a pectin lyase.
28. Use of a composition according to claim 1 [any of the preceding claims] for the removal of plant-, dirt-based stains, highly coloured food soils/stains and body soils.
29. Use of a composition according to claim 1 [any of the preceding claims] for superior fabric whiteness maintenance.
30. Use of a composition according to claim 11 [claims 5-11] for effective highly coloured stains and soils removal on plasticware, and/or for preventing the staining and/or discolouration of the dishware by highly coloured components.

5 DETERGENT COMPOSITIONS COMPRISING A PECTATE LYASE AND A BLEACH SYSTEM

10

15

**Field of the Invention**

20

The present invention relates to detergent compositions comprising a pectate lyase and a bleach system selected from : a combination of a colour safe bleach booster and a peroxygen source, a metal bleach catalyst and/or a diacyl peroxide.

25

**Background of the invention**

30

Performance of a detergent product is judged by a number of factors, including the ability to remove soils, and the ability to prevent the redeposition of the soils, or the breakdown products of the soils on the articles in the wash. Therefore, detergent compositions include nowadays a complex combination of active ingredients which fulfill certain specific needs. In particular, current detergent formulations generally include surfactants and detergent enzymes providing cleaning and fabric care benefits.

35

Removal of stains stemming from plants, wood, mould-clay based soils, muddy soils, and fruits is one of today's toughest cleaning task; especially with the trend toward low wash temperatures. These stains typically contain complex mixtures

of fibrous material based mainly on carbohydrates and their derivatives : fibres and cell wall components. Plant based soils are additionally accompanied with amylose, sugars and their derivatives. Food soils are often difficult to remove effectively from a soiled substrate. Highly coloured or "dried-on" soils derived from fruit and/or vegetable juices are particularly challenging to remove. Specific examples of such soils would include orange juice, tomato juice, banana, mango or broccoli soils. Indeed, pectin polymers are important constituents of plant cell walls. Pectin is a hetero-polysaccharide with a backbone composed of alternating homogalacturonan (smooth regions) and rhamnogalacturonan (hairy regions). The smooth regions are linear polymers of 1,4-linked alpha-D-galacturonic acid. The galacturonic acid residues can be methyl-esterified on the carboxyl group to a varying degree, usually in a non-random fashion with blocks of polygalacturonic acid being completely methyl-esterified. The substrates on which pectin containing stains are commonly found can be fabrics, dishware or hard surfaces.

In addition, highly coloured or 'dried-on' soils derived for example, from fruit and/or vegetables are also particularly challenging soils to remove. These coloured stains contain highly coloured compounds based on carotenoid compounds such as  $\alpha$ -,  $\beta$ - and  $\gamma$ -carotene and lycopene and xanthophylls (zeaxanthin or capsanthin), or porphyrins such as chlorophyll and flavonoid pigments and dye components. This latter group of natural flavonoid based dye components comprises the highly coloured anthocyanins dyes and pigments based on pelargonidin, cyanidin, delphinidin and their methyl esters and the antoxanthins. These compounds are the origin of most of the orange, red, violet and blue colours occurring in fruits and are abundant in all berries, cherry, red and black currents, grapefruits, passion fruit, oranges, lemons, apples, pears, pomegranate, red cabbage, red beets and also flowers. Carotenoids soils are derived from carrots and tomatoes and in any processed products containing these components as well as certain tropical fruits and saffron.

In particular in the dishwashing context, these coloured food soils may be removed from soiled articles into the wash solution, and then may be redeposited from the wash solution onto other articles in the wash or onto the interior of the dishwashing machine. The problem is particularly noticeable when the wash load includes articles soiled by foods naturally containing significant levels of coloured dyestuff molecules, including for example tomato sauce and curry.

The Applicant has found that plastic articles in the wash, and especially areas of the interior of the dishwashing machine which are made of plastic material, are particularly susceptible to the staining/discoloration of the dishware by coloured food soils. Said soils can interact with the surface of such plastic substrates producing staining which can be very difficult to remove.

A number of the Applicant's co-pending European Patent Applications have proposed solutions to solve the problem of coloured food dyestuff deposition in a machine dishwashing method. For example, EP 692 947 provides an efficient dye transfer inhibiting composition for use in a machine dishwashing method.

The composition comprises an enzymatic system capable of generating hydrogen peroxide in combination with certain metallo catalysts. EP 740 521 describes the use of diacyl and tetraacyl peroxide bleaching species for inhibiting the transfer of bleachable food soils and enhancing their removal from plastic substrates.

Furthermore, the complex nature of everyday "body" soils typically found on pillow cases, T-shirts, collars and socks, provides a continuous thorough cleaning challenge for detergents. These soils are difficult to remove completely due in part to their interaction with the pectin components in the primary cell walls of cotton fibers comprising cotton containing fabrics, and often residues build up on such fabric leading to dinginess and yellowing. Moreover, body fluid stains, such as blood and menstrual fluids, are often difficult to remove effectively from a soiled item, especially when the stains have been aged. Everyday body soils are also found on sanitary and kitchen surfaces such as bathtubs, toilet bowls and dishware.

Bleaching compositions for the bleaching of such plant-, dirt based stains, highly coloured stains and soils and body soils, have been extensively described in the art. Suitable bleaching agents are usually percompounds which liberate hydrogen peroxide in aqueous solution, such as peroxyhydrates, perborate, percarbonate, perpyrophosphate, persilicate, urea peroxide and the like. It is known that the use of such percompounds can be improved by the use of organic bleach activators or peroxyacid precursors. Such bleaching compositions are known to be effective in the removal of all sorts of stains. More recently, products containing bleach catalysts, particularly manganese bleach catalysts have become of interest.

In addition, oxygen bleaching agents have become increasingly popular in recent years in household and personal care products to facilitate stain and soil removal. Bleaches are particularly desirable for their stain-removing, dingy fabric cleanup, whitening and sanitization properties. Oxygen bleaching agents have found particular acceptance in laundry products such as detergents, in automatic dishwashing products and in hard surface cleansers. Oxygen bleaching agents, however, are somewhat limited in their effectiveness. Some frequently encountered disadvantages include colour damage on fabrics and damage to laundry appliances, specifically rubber hoses these appliances may contain. In addition, oxygen bleaching agents tend to be extremely temperature rate dependent. Thus, the colder the solution in which they are employed, the less effective the bleaching action. Temperatures in excess of 60°C are typically required for effectiveness of an oxygen bleaching agent in solution.

Attempts have been made to develop a bleach system which will be effective in lower temperature water conditions. U.S. Patent No. 5,360,568 to Madison et al., U.S. Patent No. 5,360,569 to Madison et al., and U.S. Patent No. 5,370,826 to Madison et al., all relate to positively charged quaternary imine salts as catalysts for peroxygen compounds to transfer active oxygen and thus are said to increase the activity of peroxygen compounds over a range of water temperatures, including lower temperatures. However, these positively charged quaternary imine salts are not completely satisfactory in laundry bleaching applications. In particular, the positively charged quaternary imine salts disclosed in these references, when combined with peroxygen compounds, cause an unacceptable level of colour damage on fabrics.

Accordingly, the need remains for a detergent compositions providing effective bleaching, especially of plant-, dirt based stains, highly coloured stains and soils and body soils. Such need is even more accute in lower water temperatures and while providing improved colour-safety profiles and/or preventing the staining /discoloration of dishware by highly coloured components. These needs are met by the detergent compositions of the present invention comprising a pectate lyase enzyme and a bleach system selected from : a combination of a bleach booster and a peroxygen source, a metal bleach catalyst and/or a diacyl peroxide.

It has been surprisingly found that such selected bleach systems can maximise the pectate lyase enzyme cleaning efficiency. Further it has been surprisingly found that detergent compositions comprising a pectate lyase and a such selected bleach system, provide superior cleaning due to the synergistic effect of the selected bleach system providing cleaning, stain removal and in a laundry context whiteness maintenance, and the pectate lyase degrading the pectin components of such soil and/or, in a laundry context, the pectin component of the fabrics that can bind such soils. These selected bleach systems - enzyme mixed systems deliver an outstanding cleaning effect, especially on food coloured stains and body soils. Moreover, when formulated as a laundry and/or fabric care composition, the compositions of the present invention provide synergistic whiteness maintenance.

Without wishing to be bound by theory, it is believed that the natural pectins found in many common fruit and vegetable based soils as well as the primary wall of cotton fibers attract and hold soil residues, particularly highly colored soil components. Removal of the pectin component with pectate lyase exposes these color bodies to the bleach system. It is believed that the synergistic effect is due to these bleach systems decolourizing the colour components of tough to remove food stains and body soils and the pectate lyase degrading the pectin components of such soil and/or in a laundry context. the pectin components of the fabrics that can bind or otherwise interact with such soils, making said soils difficult to remove.

In particular, it has been surprisingly found that the detergent compositions of the present invention comprising a diacyl peroxide, provide effective stain removal, especially on highly coloured stains and soils, especially on plasticware, and further prevent the staining / discoloration of the dishware by highly coloured components. Furthermore, it has been surprisingly found that the combination of a pectate lyase with the bleach booster as the selected bleach system, enhances cleaning by improving the overall efficiency of the bleach system, especially at low wash temperatures. The addition of a bleach booster enables the oxygen-based bleaching system to more thoroughly bleach these exposed color bodies at low wash temperatures resulting in both improved stain removal and enhanced whiteness.

Pectin degrading enzymes are known to provide soil/stain removal benefits when used in washing and cleaning operations, specifically to provide the removal of a broad range of plant and fruit based stains and enhance the body soil cleaning profile of the detergent compositions. By pectin degrading enzyme it is meant  
5 herein any enzyme which acts to break down pectin substances and pectin related substances. Pectin degrading enzymes can be classified according to their preferential substrate, highly methyl-esterified pectin or low methyl-esterified pectin and polygalacturonic acid (pectate), and their reaction mechanism, beta-elimination or hydrolysis. Pectin degrading enzymes can be mainly endo-acting,  
10 cutting the polymer at random sites within the chain to give a mixture of oligomers, or they may be exo-acting, attacking from one end of the polymer and producing monomers or dimers. Several pectinase activities acting on the smooth regions of pectin are included in the classification of enzymes provided by the Enzyme Nomenclature (1992) such as pectate lyase (EC 4.2.2.2), pectin  
15 lyase (EC 4.2.2.10), polygalacturonase (EC 3.2.1.15), exo-polygalacturonase (EC 3.2.1.67), exo-polygalacturonate lyase (EC 4.2.2.9) and exo-poly-alpha-galacturonosidase (EC 3.2.1.82). The pectin degrading enzymes are natural mixtures of the above mentioned enzymatic activities.

20 Each type of pectin degrading enzyme has a unique profile of substrate specificity, activity and stability under different hardness, pH, temperature, surfactant and other detergent ingredient matrix conditions. Pectin degrading enzymes are specifically directed to degrade pectin substances and in particular plant cell walls. In particular, pectate lyase enzymes are directed to the cleavage  
25 of  $\alpha$ -D-(1,4) glycosidic bonds in poly-D-galacturonans by the mechanism of  $\beta$ -elimination. These pectate lyase enzymes further help as well the removal of mixed stains / soils comprising pectin substances and other components. However, soils / stains which are not sensitive to pectate lyases such as non-pectin carbohydrates, lipids, proteins and their derivatives may block the  
30 accessibility of the pectin substances to the enzymes and necessitate a further strong detergent ingredient.

The use of pectin degrading enzymes in detergent has already been recognised in the art. The use of pectin enzyme is also recognised for the cleaning of contact  
35 lenses (US 4,710,313 - J60196724). Enzymes having a pectinase activity are described in DE 36 35 427 to increase the capacity of the detergent for removing

inorganic dirt, e.g. sludge, from laundry without damaging the fibres and without discoloration to allow the use of zeolites and polycarbonate builders which have a lower capacity for dispersing inorganic materials than the phosphates. Benefits for the use of pectin enzymes in detergent formulations, particularly those designed for use in laundry, dishwashing and household cleaning operations have been recognised in WO95/25790. JP 60226599 describes detergent compositions comprising conventional detergent actives and a cellulase and hydrolase such as hemicellulase, pectinase, amylase or protease. The combination of cellulase and hydrolase is said to give a good washing effect on inorganic fouling together with enzymatic activity. WO95/09909 describes an enzyme preparation comprising modified enzymes selected from the group of amylase, lipase, oxidoreductase, pectinase or hemicellulase; the modified enzymes having an improved performance due to an alkaline pI and/or increased surface activity obtained by chemical modification or amino acid substitution. Modified pectin and/or pectolytic and/or hemi-cellulolytic and /or lipolytic enzymes are applied advantageously in the papermaking industry and modified amylase and/or lipase in laundry and dishwashing.

In particular, Pectate lyases have been cloned from different bacterial genera such as *Erwinia*, *Pseudomonas*, *Klebsiella*, *Streptomyces*, *Penicillium*, *Bacteroides*, *Thermomonospora*, *Fusarium*, *Aspergillus* and *Xanthomonas*. Also from *Bacillus subtilis* (Nasser et al. (1993) FEBS **335**:319-326) and *Bacillus* sp. YA-14 (Kim et al. (1994) Biosci. Biotech. Biochem. **58**:947-949) cloning of a pectate lyase has been described. Purification of pectate lyases with maximum activity in the pH range of 8-10 produced by *Bacillus pumilus* (Dave and Vaughn (1971) J. Bacteriol. **108**:166-174), *B. polymyxa* (Nagel and Vaughn (1961) Arch. Biochem. Biophys. **93**:344-352), *B. stearothermophilus* (Karbassi and Vaughn (1980) Can. J. Microbiol. **26**:377-384), *Bacillus* sp. (Hasegawa and Nagel (1966) J. Food Sci. **31**:838-845) and *Bacillus* sp. RK9 (Kelly and Fogarty (1978) Can. J. Microbiol. **24**:1164-1172) has been reported. WO 98/45393 discloses detergent compositions containing protopectinase with remarkable detergency against muddy soiling.

Diacyl peroxides are widely used as polymerisation initiators, curing agents and bleaching agents. US patent No. 5,334,326 describes a liquid or paste dispersion which comprises a diaroyl peroxide, a liquid alkyl ester of benzoic acid in which



the alkyl group of the ester has from 8 to 12 carbon atoms, and water from 0-40%wt. The ratio of said diacyl peroxide to said alkyl benzoate is from 0.3:1 to 7:1. US patent No. 4,255,277 describes a non-separating catalyst paste comprising a diacyl peroxide; a minor proportion of water, a finely divided calcium carbonate in an amount sufficient to prevent the composition from physically separating into its components. US patent No. describes solid organic peroxide compositions containing from 50-70%wt of a solid organic peroxide such as dibenzoyl peroxide and a combination of liquid and solid desensitisers. US patent No. 3,723,336 discloses a non-separating composition of 20-60parts of dibenzoyl peroxide. WO96/27586 relates to a solid diacyl organic peroxide formulations in liquid or paste form having improved thermal stability. WO95/33817 describes a wax-encapsulated particle having a core particle or an aggregate of core particles selected from the group of an organic peroxy acid, a diacyl peroxide, an inorganic peroxygen compound, a bleach catalyst, a peroxygen bleach precursor and/or mixtures thereof together with 0.01-5%wt of a surfactant. GB 1 538 477 relates to bleaching compositions comprising a surfactant, a builder salt and a bleaching agent comprising a diacyl peroxide of the general formula ROOR<sub>1</sub> wherein R is a phthaloyl radical and R<sub>1</sub> an acyl radical. EP 257 700 relates to a bleaching composition comprising a percompound and a mixture of at least two selected peroxyacid bleach precursors.

Metal bleach catalysts are known in the detergency field. Recent art includes : WO98/36403 describes laundry compositions comprising a transition metal bleach catalyst comprising a complex of a transition metal and a cross-bridged macropolycyclic ligand. WO98/39405 relates to a laundry composition comprising a bleach activator and/or organic percarboxylic acid, a transition metal bleach catalyst comprising a complex of a transition metal and a cross-bridged macropolycyclic ligand. WO97/36991 relates to a bleaching composition comprising a metal-containing bleach catalyst, an oxygen-releasing bleach system and an amino tricarboxylic acid of a specific formula. WO97/34985 discloses a bleaching composition comprising a metal-containing bleach catalyst, an oxygen-releasing bleach system and a cellulase. WO97/29174 describes bleach catalyst particles for use in detergent compositions. WO97/22681 relates to an automatic dishwashing composition comprising a metal bleach catalyst, a source of hydrogen peroxide, phosphate builder and a dishwashing ingredient.

However, the synergistic combination of a pectate lyase and a selected bleach system selected from a combination of a bleach booster and a peroxygen source, a metal catalyst and/or a diacyl peroxide in a bleaching composition, for superior cleaning performance in a detergent composition, has never been previously recognised.

### **Summary of the invention**

- 10 The present invention relates to laundry, dishwashing or hard surface cleaner detergent compositions comprising a pectate lyase and a bleach system selected from : a combination of a bleach booster and a peroxygen source, a metal bleach catalys and or a diacyl peroxide.
- 15 These compositions provide superior cleaning performance, especially on plant-, dirt-based stains, highly coloured food soils/stains and body soils. Such laundry detergent compositions also provide superior whiteness maintenance. Furthermore, these compositions comprising a colour-safe booster, provide superior cleaning performance in lower water temperatures while providing improved colour-safety profiles. In addition, these compositions comprising diacyl
- 20 peroxide, provide effective highly coloured stains and soils removal, especially on plasticware, and further prevent the staining / discoloration of the dishware by highly coloured components.

25

### **Detailed description of the invention**

The detergent compositions of the present invention comprise as essential elements a pectate lyase enzyme and a bleach system selected from : a combination of a bleach booster and a peroxygen source, a metal bleach

30 catalyst and/or a diacyl peroxide.

Each type of pectin degrading enzyme has a unique profile of substrate specificity, activity and stability under different hardness, pH, temperature, surfactant and other detergent ingredient matrix conditions. Pectin degrading

35 enzymes are specifically directed to degrade pectin substances and in particular

plant cell walls. In particular, pectate lyase is a pectin degrading enzyme which splits the  $\alpha$ -1,4-glucoside bond of polygalacturonic acids found in pectin substances, to create a double bond between C4 and C5. Pectate lyase enzymes further help the removal of mixed stains / soils comprising pectin substances and other components. However, soils / stains which are not sensitive to pectate lyases such as non-pectin carbohydrates, lipids, proteins and their derivatives or highly coloured materials associated with the pectins, may block the accessibility of the pectin substances to the enzyme and necessitate a further strong detergent ingredient.

10

It has been surprisingly found that the selected bleach of the present invention can maximise the pectate lyase cleaning efficiency. Such selected bleach systems are known to provide superior cleaning and stain removal of highly coloured stains, and in a laundry and/or fabric care context, whiteness maintenance and especially greasy/oily stain removal. Without wishing to be bound by theory, it is believed that the pectate lyase degrades the pectin component of soils and stains that serves to bind colour bodies and chromophores. Such enzymatic degradation of the pectin components exposes these colour bodies and chromophores to the bleach system, allowing them to be effectively removed. It has been found that such combinations lead to performance synergy in soil and stain cleaning, especially on coloured food stains/soils and body soils.

20

In particular, it is well known in the art that cleaning performance decreases with decreasing temperatures. This is especially true for the removal of pectin-based stains/soils and the performance of oxygen bleaching systems. Not wishing to be bound by theory it is believed that pectate lyase helps to improve overall cleaning at low temperatures by catalyzing the hydrolysis of the pectin found in many soils/stains, and in a laundry context, in the residual primary wall of cotton fibers, that can trap and hold color bodies onto surfaces. Hydrolysis of the pectin allows easier removal by the rest of the detergent ingredients. Improved removal of the pectin component of highly colored food stains as well as the pectin from cotton fibers exposes soil chromophores to the oxygen bleaching system in the detergent formulation. Bleach booster enhances performance of the oxygen bleach system at low temperatures. The combination of a pectate lyase with a bleach booster in a detergent formulation containing an oxygen bleaching

35

system, provides an effective means of removing high colored food soils from dishware and fabric surfaces and, in a laundry context, effective removal of body soils from fabric surfaces.

## 5 The Pectate Lyase enzyme

An essential element of the detergent composition of the present invention is a pectate lyase enzyme.

- 10 Pectate lyase is classified within the classification of enzymes provided by the Enzyme Nomenclature (1992) as EC 4.2.2.2. Said enzyme is known to split the  $\alpha$ -1,4-glucoside bond of galacturonic acid found in pectin substances, creating a double bond between C4 and C5 and is substantially free for other pectin degrading activities, i.e having less than 25%, preferably less than 15%, more  
15 preferably less than 5% by weight of the enzyme compound of other pectin degrading enzyme activities.

- Pectate lyases have been cloned from different bacterial genera such as *Erwinia*, *Pseudomonas*, *Klebsiella*, *Streptomyces*, *Penicillium*, *Bacteroides*,  
20 *Thermomonospora*, *Fusarium*, *Aspergillus* and *Xanthomonas*. Also from *Bacillus subtilis* (Nasser et al. (1993) FEBS **335**:319-326) and *Bacillus* sp. YA-14 (Kim et al. (1994) Biosci. Biotech. Biochem. **58**:947-949) cloning of a pectate lyase has been described. Purification of pectate lyases with maximum activity in the pH range of 8-10 produced by *Bacillus pumilus* (Dave and Vaughn (1971) J.  
25 Bacteriol. **108**:166-174), *B. polymyxa* (Nagel and Vaughn (1961) Arch. Biochem. Biophys. **93**:344-352), *B. stearothermophilus* (Karbassi and Vaughn (1980) Can. J. Microbiol. **26**:377-384), *Bacillus* sp. (Hasegawa and Nagel (1966) J. Food Sci. **31**:838-845) and *Bacillus* sp. RK9 (Kelly and Fogarty (1978) Can. J. Microbiol. **24**:1164-1172) has been reported. WO 98/45393 discloses detergent  
30 compositions containing protopectinase with remarkable detergency against muddy soils.

- Further suitable pectate lyases for use in the present invention are the protopectinases having an optimum reaction pH of 7.0 or higher when  
35 polygalacturonic acid is used as a substrate such as described in WO98/45393 and the pectic acid lyase having the amino acid sequence SEQ no 1 of EP 870

843 or having such amino acid sequence with one or more amino acid being deleted, added or substituted.

Preferred are the pectate lyase enzymes described in the international co-pending application PCT/DK98/00515, internationally filed on November 24, 1998 and published under WO 99/27084:

- A pectate lyase comprising a first amino acid sequence consisting of seven (7) amino acid residues having the following sequence: Asn Leu Asn Ser Arg Val Pro (NLNSRVP);

- A pectate lyase which is :

- 5           i) a polypeptide produced by *Bacillus agaradhaerens*, NCIMB 40482 or DSM 8721, or by a *Bacillus* species having a 16S rDNA sequence homology to *Bacillus agaradhaerens*, DSM 8721, of at least 99%, or
- ii) a polypeptide comprising an amino acid sequence as shown in positions 27-359 of SEQ ID NO:2 of PCT/DK98/00515, or
- 10          iii) an analogue of the polypeptide defined in i) or ii) which is at least 45% homologous with said polypeptide, or
- iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 240, and optionally also the arginine in position 245, is conserved and the derived
- 15          polypeptide is at least 42% homologous with said polypeptide, or
- v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form;

- A pectate lyase which is :

- 20           i) a polypeptide produced by *Bacillus licheniformis*, ATCC 14580, or by a *Bacillus* species having a 16S rDNA sequence homology to *Bacillus licheniformis*, ATCC 14580, of at least 99%, or
- ii) a polypeptide comprising an amino acid sequence as shown in positions 28-341 of SEQ ID NO:4 of PCT/DK98/00515, or
- 25          iii) an analogue of the polypeptide defined in i) or ii) which is at least 45% homologous with said polypeptide, or
- iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 233, and optionally also the arginine in position 238, is conserved and the derived polypeptide is at least 42% homologous with said polypeptide, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form;

- A pectate lyase which is :

- 5 i) a polypeptide produced by a *Bacillus* species having the 16S rDNA sequence of SEQ ID NO:14 of PCT/DK98/00515 or by a *Bacillus* species having a 16S rDNA sequence homology to SEQ ID NO:14 of PCT/DK98/00515 higher than 97.3%; or
- 10 ii) a polypeptide comprising an amino acid sequence as shown in positions 181-509 of SEQ ID NO:6 of PCT/DK98/00515, or
- 15 iii) an analogue of the polypeptide defined in i) which is at least 50% homologous with said polypeptide, or
- iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 390, and optionally also the arginine in position 395, is conserved and the derived polypeptide is at least 44% homologous with said polypeptide, or
- v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form,

- A pectate lyase which is :

- 20 i) a polypeptide produced by the species *Bacillus halodurans*, or
- ii) a polypeptide comprising an amino acid sequence as shown in positions 42-348 of SEQ ID NO:8 of PCT/DK98/00515, or
- 25 iii) an analogue of the polypeptide defined in i) or ii) which is at least 45% homologous with said polypeptide, or
- iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 240, and optionally also the arginine in position 245, is conserved and the derived polypeptide is at least 40% homologous with said polypeptide, or
- v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form,

30 - A pectate lyase which is

- i) a polypeptide produced by a *Bacillus* species having the 16S rDNA sequence of SEQ ID NO:13 of PCT/DK98/00515 or by a *Bacillus* species having a 16S rDNA sequence homology to SEQ ID NO:13 of PCT/DK98/00515 higher than 98.1%; or
- 35 ii) a polypeptide comprising an amino acid sequence as shown in positions 25-335 of SEQ ID NO:10 of PCT/DK98/00515, or

- iii) an analogue of the polypeptide defined in i) or which is at least 45% homologous with said polypeptide, or
- iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 227, and optionally also the arginine in position 232, is conserved and the derived polypeptide is at least 41% homologous with said polypeptide, or
- v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

10 Similarly preferred is the pectate lyase enzyme described in international co-pending application PCT/DK98/00514, internationally filed on November 24, 1998 and published under WO99/27083 and which is :

- i) a polypeptide produced by *Bacillus licheniformis*, ATCC 14580, or
- ii) a polypeptide comprising an amino acid sequence as shown in positions 28-221 of SEQ ID NO:4 of PCT/DK98/00514, or
- iii) an analogue of the polypeptide defined in i) or ii) which is at least 60% homologous with said polypeptide, or
- iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the lysines in positions 133 and 155 and the arginine in position 158 are conserved and the derived polypeptide is at least 66% homologous with positions 60-158 of SEQ ID NO:4 of PCT/DK98/00514, or
- v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

25 More preferred pectate lyases for the purpose of the present invention are those having optimum activity at pH's >7.0 and derived from *Streptomyces fradiae*, *Streptomyces nitrosporeus*, *Erwinia carotovora*, *Bacillus sphaeroides*, *Thermomonospora fusca*, *Pseudomonas solanacearum*, *Bacteroides* *thetaiotaomicron*, *Fusarium solani*, *Xanthomonas campestris*, *Bacillus* *agaradhaerens*, and/or *Bacillus licheniformis*.

30 Most preferred pectate lyase for the purpose of the present invention is the Pectate lyase from *Bacillus agaradhaerens*, NCIMB 40482 or DSM 8721.

The pectate lyase is incorporated into the detergent compositions of the present invention preferably at a level of from 0.0001% to 2%, more preferably from 0.0005% to 0.1%, most preferred from 0.001% to 0.02% pure enzyme by weight of the composition.

5

The pectate lyase of the invention, in addition to the enzyme core comprising the catalytically domain, may also contain a cellulose binding domain (CBD), the cellulose binding domain and enzyme core (the catalytically active domain) of the enzyme being operably linked. The cellulose binding domain (CBD) may exist as an integral part of the encoded enzyme, or a CBD from another origin may be introduced into the enzyme thus creating an enzyme hybrid. In this context, the term "cellulose-binding domain" is intended to be understood as defined by Peter Tomme et al. "Cellulose-Binding Domains: Classification and Properties" in "Enzymatic Degradation of Insoluble Carbohydrates", John N. Saddler and Michael H. Penner (Eds.), ACS Symposium Series, No. 618, 1996. This definition classifies more than 120 cellulose- binding domains into 10 families (I-X), and demonstrates that CBDs are found in various enzymes such as cellulases, xylanases, mannanases, arabinofuranosidases, acetyl esterases and chitinases. CBDs have also been found in algae, e.g. the red alga *Porphyra purpurea* as a non-hydrolytic polysaccharide-binding protein, see Tomme et al., op.cit. However, most of the CBDs are from cellulases and xylanases, CBDs are found at the N and C termini of proteins or are internal. Enzyme hybrids are known in the art, see e.g. WO 90/00609 and WO 95/16782, and may be prepared by transforming into a host cell a DNA construct comprising at least a fragment of DNA encoding the cellulose- binding domain ligated, with or without a linker, to a DNA sequence encoding the pectate lyase enzyme and growing the host cell to express the fused gene. Enzyme hybrids may be described by the following formula:

CBD - MR - X

wherein CBD is the N-terminal or the C-terminal region of an amino acid sequence corresponding to at least the cellulose binding domain; MR is the middle region (the linker), and may be a bond, or a short linking group preferably of from about 2 to about 100 carbon atoms, more preferably of from 2 to 40 carbon atoms; or is preferably from about 2 to about 100 amino acids, more preferably of from 2 to 40 amino acids; and X is an N-terminal or C-terminal region of the pectate lyase of the invention.



5 The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimise their performance efficiency in the detergent compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

10

15 In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing metal binding sites to increase chelant stability.

20

### **The bleach system**

25 The detergent compositions of the present invention further comprise a bleach system selected from : a combination of a bleach booster and a peroxygen source, a metal bleach catalyst and/or a diacyl peroxide, as a second essential element.

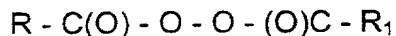
### **The Diacyl Peroxide bleach system**

30 The bleach system encompassed in the compositions of the present invention can be a diacyl peroxide (or DAP). Said diacyl peroxide can be liquid and is preferably incorporated in this form, into liquid detergent compositions or can be

35

comprised into a particulate and is preferably included in such form. into granular detergent compositions.

- 5 The DAP may be selected from the group consisting of dialiphatic peroxide, diaromatic peroxide, aliphatic-aromatic peroxide or mixtures thereof and are of the general formula :



- 10 wherein R and R<sub>1</sub> can be the same or different and are selected from either aliphatic or aromatic groups having from 6 to 20 carbon atoms.

The DAPs of the present invention are selected from the group consisting of dialiphatic peroxide, diaromatic peroxide, aliphatic-aromatic peroxide and mixtures thereof.

- 15 Where R and/or R<sub>1</sub> is an aliphatic group it may be branched, but is preferably linear. Preferred aliphatic groups have from 8 to 14 carbon atoms, most preferably 10 to 12 carbon atoms. Particularly, preferred dialiphatic peroxides include dioctanoyl peroxide, didecanoyl peroxide, dilauroyl peroxide, dimyristoyl peroxide or mixtures thereof. Dilauroyl peroxide is available from Akzo Nobel under the tradename Laurox®. Dodecanoyl peroxide is available from Akzo Nobel under the tradename Perkadox SE 10.

- 20 Preferred DAP's are aliphatic-aromatic peroxides wherein one of either R or R' is aliphatic and the other is aromatic. In these species the aromatic moiety is preferably benzoyl. In an alternative embodiment, the aromatic species may be a substituted benzoyl wherein the substituent is preferably an alkyl group having from 1 to 20 carbon atoms. The aliphatic moiety preferably comprises from 8 to 25 14 carbon atoms, more preferably from 10 to 12 carbon atoms and although it may be branched, it is preferably linear.

Examples of suitable diacyl peroxides are dibenzoyl peroxide, benzoyl glutaryl peroxide, benzoyl succinyl peroxide, di-(2-methylbenzoyl) peroxide, diphtaloyl peroxide, dioctanoyl peroxide, didecanoyl peroxide, dilauroyl peroxide, dimyristoyl peroxide, benzoyl lauroyl peroxide, substituted benzoyl lauroyl peroxide and mixtures thereof. Preferred diacyl peroxides are dibenzoyl peroxide,

diphtaloyl peroxides and mixtures thereof and more preferred diacyl peroxide is dibenzoyl peroxide.

More preferred for the purpose of the present invention are the dilauroyl peroxid, dibenzoyl peroxide and/or mixtures thereof.

- 5 In the instance, DAP is included in the detergent compositions of the present invention in the form of a particulate, such particulate comprises, by weight of said particulate, from 1-80% of a water-insoluble diacyl peroxide and from 0.01% to 95% stabilising additive in which the diacyl peroxide does not dissolve. Examples of suitable additives are inorganic salts, transition metal chelants, 10 antioxidants, binding agents, coatings agents and/or mixtures thereof.

- The term "Diacyl peroxide does not dissolve" is defined herein to mean the diacyl peroxide does not dissolve in the stabilising additive(s) under particulate processing conditions and/or detergent storage conditions. The Term "Water 15 insoluble" is defined herein to mean limited water solubility, i.e. less than 1%, preferably less than 0.5%, dissolves in water. The term "stabilising additive" is defined herein to mean a compound or compound(s) the prevents the diacyl peroxide from decomposing with other ingredients, especially components in which the diacyl peroxide is soluble in and with which the diacyl peroxide will 20 reacted while stored in the product.

- Said particle provide storage stability and protect the diacyl peroxide from interacting with other ingredients and decomposing in the composition over time. The stabilizing additive in the particle is by weight of the particle from about 0.1% 25 to about 95%, preferably from about 10% to about 95%, more preferably from about 40% to about 95% stabilizing additive.

- Preferably, the stabilizing additive is not miscible with other components of the composition at temperatures at or below 100°F, preferably 120°F. In a particularly preferred embodiment the stabilizing agent would be soluble in the 30 wash solution.

The inorganic salt, useful as a stabilizing additive include but are not limited to alkali metal sulfates, citric acid, and boric acid, and their salts, alkali metal carbonates, bicarbonates and silicates and mixtures thereof. Preferred

inorganic salts are sodium sulfate and citric acid. which, because they are non-alkaline, prevent alkaline hydrolysis in product.

Binding agents and coating agents include but are not limited to certain water soluble polymers in which the diacyl peroxide does not dissolve, ethoxylated  
5 C16-C20 alcohols with sufficient ethoxylate groups to prevent dissolution of the diacyl peroxide, aliphatic fatty acids, aliphatic fatty alcohols, maltodextrins, dextrin, starch, gelatin, polyethylene glycols with melting points above 100°F, polyvinyl alcohol, and sorbitol. The polymers include polyacrylates with an average molecular weight of from about 1,000 to about 10,000, and  
10 acrylate/maleate or acrylate/ fumarate copolymers with an average molecular weight of from about 2,000 to about 80,000 and a ratio of acrylate to maleate or fumarate segments of from about 30:1 to about 1:2. Examples of such copolymers based on a mixture of unsaturated mono- and dicarboxylate monomers are disclosed in European Patent Application No. 66,915, published  
15 December 15, 1982, incorporated herein by reference. Other suitable copolymers are modified polyacrylate copolymers as disclosed in U.S. Patents 4,530,766, and 5,084,535, both incorporated herein by reference.

Transition metal chelants which can be employed are selected from the group consisting of polyacetate and polycarboxylate builders such as the sodium,  
20 potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine tetraacetic acid, ethylenediamine disuccinic acid (especially the S,S- form), nitrilotriacetic acid, tartrate monosuccinic acid, tartrate disuccinic acid, oxydisuccinic acid, carboxymethyloxysuccinic acid, mellitic acid, sodium benzene polycarboxylate salts; nitrilotris(methylenephosphonic acid)  
25 diethylenetrinitrilopentakis(methylenephosphonic acid), 1-hydroxyethylidene-1,1-diphosphonic acid, other phosphonates chelants (e.g. Dequest line of products from Monsanto), ethylene-N,N'-bis(o-hydroxyphenylglycine), dipicolinic acid and mixtures thereof.

Antioxidants (radical trap, radical scavenger or free radical inhibitor) can also be  
30 suitable stabilizing additives. These compounds slow down or stop a reaction even though present in small amounts. In the present invention it is believed the antioxidant would trap or scavenge the radical formed due to thermal decomposition of the peroxide bond. This would prevent the radical from further reacting or propagating the formation of another radical (self-accelerated  
35 decomposition). Since this material would be used in small amounts in the particle, it most likely would not hurt overall performance of the detergent

composition. Suitable antioxidants include but are not limited to citric acid, phosphoric acid, BHT, BHA,  $\alpha$ -tocopherol, Irganox series C (Ciba Giegy), Tenox series (Kodax) and mixtures thereof..

It can be noted that of the above listed stabilizing additives can also provide other  
5 benefits in a detergent product (i.e. pH control, carbonate/silicate dispersion) as well as serve as the stabilizing additive. These ingredients therefore may also be added separately from the particulate. For example, agglomerated forms of the present invention may employ aqueous solutions of the polyacrylates discussed herein above as liquid binders for making the agglomerate.

10 The diacyl peroxide particles formed preferably have a mean particle size from about 400 $\mu$ m to about 1000 $\mu$ m, more preferably from about 600 $\mu$ m to about 800 $\mu$ m with less than 1% of the diacyl peroxide particle population being greater than 1180 $\mu$ m (Tyler 14 mesh) and less than 1% less than or equal to 212 $\mu$ m  
15 (Tyler 65 mesh).

Typically, diacyl peroxide is added to the detergent compositions of the present invention at a level of from 0.01% to 20% by weight of the composition, preferably 0.5% to 10%, more preferably 0.2% to 3%. When the diacyl peroxide  
20 is incorporated into a particulate, the compositions of the present invention comprise by weight of the composition from 0.1% to 30%, preferably from 1% to 15%, more preferably from 1.5% to 10% of diacyl peroxide particle.

Preformed diacyl peroxides are also contemplated within the present invention,  
25 such as described in EP 257 700. Also suitable are the diaroyl peroxides with improved chemical stability as described in US patent No. 5,334,326 and the solid diacyl organic peroxide dispersions disclosed in WO96/27856.

#### The Metal Bleach Catalyst

30 The bleach system encompassed in the detergent compositions of the present invention can be a metal bleach catalyst. When the detergent composition of the invention comprise a metal bleach catalyst, they will preferably comprise an peroxygen source (also called oxygen source or oxygen bleach source) as  
35 described below, defining altogether a bleaching system.

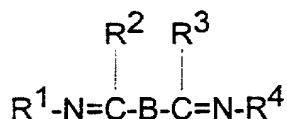
A suitable type of bleach catalyst is a catalyst comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminium cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Preferred types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include  $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$ ,  $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$ ,  $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_2$ ,  $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$ , and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

The bleach catalysts useful in the compositions herein may also be selected from the suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as  $\text{Mn}(1,4,7\text{-trimethyl-1,4,7-triaza-cyclononane})(\text{OCH}_3)_3(\text{PF}_6)$ .

Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulcitol, mannitol, xylitol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

U.S. Pat. 5,114,611 describes other suitable bleach catalysts comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with a non-(macro)-cyclic ligand. Said ligands are of the formula:



wherein  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  can each be selected from H, substituted alkyl and aryl groups such that each  $R^1-N=C-R^2$  and  $R^3-C=N-R^4$  form a five or six-membered ring. Said ring can further be substituted. B is a bridging group selected from O, S,  $CR^5R^6$ ,  $NR^7$  and  $C=O$ , wherein  $R^5$ ,  $R^6$ , and  $R^7$  can each be H, alkyl, or aryl groups, including substituted or unsubstituted groups. Preferred ligands include pyridine, pyridazine, pyrimidine, pyrazine, imidazole, pyrazole, and triazole rings. Optionally, said rings may be substituted with substituents such as alkyl, aryl, alkoxy, halide, and nitro. Particularly preferred is the ligand 2,2'-bispyridylamine. Preferred bleach catalysts include Co, Cu, Mn, Fe, -bispyridylmethane and -bispyridylamine complexes. Highly preferred catalysts include  $Co(2,2'\text{-bispyridylamine})Cl_2$ ,  $Di(\text{isothiocyanato})\text{bispyridylamine-cobalt (II)}$ ,  $tris(\text{pyridylamine-cobalt(II)})\text{ perchlorate}$ ,  $Co(2,2'\text{-bispyridylamine})_2O_2ClO_4$ ,  $Bis(2,2'\text{-bispyridylamine})\text{ copper(II) perchlorate}$ ,  $tris(\text{di-2-pyridylamine})\text{ iron(II) perchlorate}$ , and mixtures thereof.

Preferred examples include binuclear Mn complexes with tetra-N-dentate and bi-N-dentate ligands, including  $N_4Mn^{III}(u-O)_2Mn^{IV}N_4)^+$  and  $[Bipy_2Mn^{III}(u-O)_2Mn^{IV}bipy_2]-(ClO_4)_3$ .

Other bleach catalysts are described, for example, in European patent application, publication no. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts) and U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations). Highly preferred catalysts are described in U.S. 4,728,455 (manganese gluconate catalysts).

Suitable examples of manganese catalysts containing organic ligands are described in US-A-4,728,455, US-A-5,114,606, US-A-5,153,161, US-A-5,194,416, US-A-5,227,804, US-A-5,246,612, US-A-5,246,621, US-A-5,256,779, US-A-5,274,147, US-A-5,280,117, and EP-A-544,440, EP-A-544,490, EP-A-549,271 EP-A-549,272. Preferred examples of these catalysts include  $\text{Mn}^{\text{IV}}_2(\text{u-O})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$ ,  $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$ ,  $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_4(\text{ClO}_4)_4$ ,  $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$ ,  $\text{Mn}^{\text{IV}}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})\text{(OCH}_3)_3(\text{PF}_6)$ , and mixtures thereof. Other metal-based bleach catalysts include those disclosed in US-A-4,430,243 and US-A-5,114,611.

Iron and manganese salts of aminocarboxylic acids in general are useful herein including iron and manganese amino-carboxylate salts disclosed for bleaching in the photographic color processing arts. A particularly useful transition metal salt is derived from ethylenediaminedisuccinate and any complex of this ligand with iron or manganese.

Another type of bleach catalyst, as disclosed in US-A-5,114,606, is water soluble complex of manganese (II), (III)m and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulcitol, mannitol, xylitol, arabitol, adonitol, meso-erythritol, meso-inositolm, lactose and mixtures thereof. Especially preferred is sorbitol.

Other examples include Mn gluconate,  $\text{Mn}(\text{CF}_3\text{SO}_3)_2$ , and binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including  $[\text{bipy}_2\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{bipy}_2](\text{ClO}_4)_3$ .

Other bleach catalysts are described, for example, in EP-A-408,131 (cobalt complexes), EP-A-384,503 and EP-A-306,689 (metallo-porphyrins), US-A-4,728,455 (manganese/multidentate ligand), US-A-4,711,748 (adsorbed manganese on aluminosilicate), US-A-4,601,845 (aluminosilicate support with manganese, zinc or magnesium salt), US-A-4,626,373 (manganese/ligand), US-A-4,119,557 (ferric complex), US-A-4,430,243 (Chelants with manganese cations and non-catalytic metal cations), and US-A-4,728,455 (manganese gluconates).



Other suitable Metal-containing catalysts for use in the present invention include cobalt-containing catalysts such as Pentaamine acetate cobalt(III) salts and manganese-containing catalysts such as those described in EPA 549 271; EPA 549 272; EPA 458 397; US 5,246,621; EPA 458 398; US 5,194,416 and US 5,114,611. Bleaching composition comprising a peroxy compound, a manganese-containing bleach catalyst and a chelating agent is described in the patent application No 94870206.3 published under EP-A-718 398.

Preferred catalysts are the catalysts based on cobalt and described in WO96/23859, WO96/23860 and WO96/23861 and US-A-5,559,261. WO 96/23860 describe cobalt catalysts of the type  $[Co_n L_m X_p]^Z Y_z$ , where L is an organic ligand molecule containing more than one heteroatom selected from N,P,O and S; X is a co-ordinating species; n is preferably 1 or 2; m is preferably 1 to 5; p is preferably 0 to 4 and Y is a counterion. One example of such a catalyst is  $Nm N'$ -Bis(salicylidene)ethylenediaminecobalt (II). Other cobalt catalysts described in these applications are based on Co(III) complexes with ammonia and mon-, bi-, tri- and tetradentate ligands such as  $[Co(NH_3)_5 OAc]^{2+}$  with  $Cl^-$ ,  $Oac^-$ ,  $PF_6^-$ ,  $SO_4^{=}$ ,  $BF_4^-$  anions. Preferred cobalt catalysts are the one described in US 5,798,326 and US 5, 703,030. US 5,798,326 describes a selection of cobalt (III) catalysts having the formula :  $Co[(NH_3)_n M_m B_b T_t Q_q P_p] Y_y$  wherein Cobalt is in the +3 oxidation from, n is an integer from 0 to 5, preferably 4-5, more preferably 5; M represents a monodentate ligand; m is an integer from 0-5, preferably 1 or 2, more preferably 1; B represents a bidentate ligand; b is an integer from 0-2; T represents a tridentate ligand; t is 0 or 1; Q is a tetradentate ligand; q is 0 or 1; P is an pentadentate ligand; p is 0 or 1 and  $n+m+2b+3t+4q+5p=6$ ; Y is one or more appropriately selected counteranions present in a number y, where y is an integer from 1-3, preferably 2-3, more preferably 2 when Y is a -1 charged anion, to obtain a charge-balanced salt. US 5,703,030 describes a cobalt catalyst having the formula  $[Co(NH_3)_5 M] T_y$  wherein cobalt is in the +3 oxidation state; M is a carboxylate-containing ligand having the formula  $RC(O)O^-$ ; and T is one or more counteranions present in a number y, where y is an integer to obtain a charge-balanced salt (preferably from 1-3, more preferably 2 when T is a -1 charged anion).

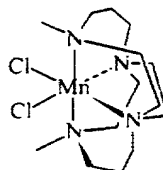
Certain transition-metal containing bleach catalysts can be prepared in situ by the reaction of a transition-metal salt with suitable chelating agent for example a mixture of manganese sulfate and ethylenediaminediscussinate. Highly coloured transition metal-containing bleach catalysts may be co-processed with zeolites to  
 5 reduce the colour impact.

Preferred metal catalysts for the purpose of the present invention are the catalysts described in WO98/39406 and comprising a complex of a transition metal and a cross-bridged macropolycyclic ligand in which:

- 10 (1) the metal is selected from Mn(II), Mn(IV), Mn(V), Fe(II), Fe(III), Fe(IV), Co(I), Co(II), Co(III), Ni(I), Ni(II), Ni(III), Cu(I), Cu(II), Cr(III), Cr(IV), Cr(V), Cr(VI), V(III), V(IV), V(V), Mo(IV), Mo(V), Mo(VI), W(IV), W(VI), Pd(II), Ru(II), Ru(III) and Ru(IV); and
- (2) the macropolycyclic rigid ligand is selected from:
  - 15 (i) ligand of formula (I) having denticity of 4 or 5;
  - (ii) ligand of formula (II) having denticity of 5 or 6;
  - (iii) ligand of formula (III) having denticity of 6 or 7; (where E = moiety (CR<sub>n</sub>)<sub>a</sub>-X-(CR<sub>n</sub>)<sub>a'</sub>; X = O, S, NR or P, or a covalent bond (especially covalent bond); for each E the sum of a + a' = 1-5 (especially 2 and 3; G = (CR<sub>n</sub>)<sub>b</sub>; R = H, alkyl, alkenyl, alkynyl, aryl, alkylaryl or heteroaryl or two or more are covalently bonded to form an aromatic or hetero aromatic, cycloalkyl or heterocycloalkyl ring; D = donor atom selected from N, O, S, or P, at least two D atoms are bridgehead donor atoms coordinated to the transition metal; b = Cor D or cycloalkyl or heterocyclic ring; n = 1 or 2, completing the valence of C atoms to which R moieties are bonded; n' = 0 or 1 completing the valence of D donor atoms to which R moieties are bonded; n'' = 0, 1 or 2 completing the valence of B atoms to which R moieties are bonded; a, a' = 0-5, preferably a + a' = 2 or 3, the sum of all a + sum of all a' in formula (I) being 7-12, the sum of all a + a' in formula (II) being 6 (especially 8) -12, the sum of all a + a' in formula (III) being 8 (especially 10)-15 and the sum of all a + a' in formula (IV) being 10 (especially 12)-18; b = 0-9 (especially 0-5) or one or more of the (CR<sub>n</sub>)<sub>b</sub> moieties covalently bonded from any D to the B atom is absent as long as at least two (CR<sub>n</sub>)<sub>b</sub> covalently bond two of the D donor atoms to the B atom and the sum of all b is 1-5; and
- 20
- 25
- 30
- 35

(iv) optionally one or more non-macropolycyclic ligands, preferably selected from H<sub>2</sub>O, ROH, NR<sub>3</sub>, RCN, OH<sup>-</sup>, OOH<sup>-</sup>, RS<sup>-</sup>, RO<sup>-</sup>, OCN<sup>-</sup>, SCN<sup>-</sup>, N<sub>3</sub><sup>-</sup>, CN<sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, O<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, organic phosphates, organic phosphonates, organic sulphates, organic sulphonates, and aromatic N-donors such as pyridines, pyrazines, pyrazoles, imidazoles, benzimidazoles, pyrimidines, triazoles, and thiazoles with R being H, optionally substituted alkyl or aryl; and (b) at least 0.1% adjunct ingredient(s), preferably oxygen bleaching agent. Preferably the donor atoms in the macropolycyclic ligand are N, S, O or P, especially N or O, more especially all are N. The ligand comprises 4 or 5 donor atoms all connected to the same transition metal. The ligand comprises an organic macrocycle ring having at least 12, especially 12-20 atoms. All X are covalent bonds, a' are 0 and B are 0.1 or 2. The mol ratio of transition metal to ligand is 1:1 and transition metal is Mn or Fe.

More preferred catalyst comprising such complex of a transition metal and a cross-bridged macropolycyclic ligand is [Mn(Bcyclam)Cl<sub>2</sub>]:



"Bcyclam" (5,12-dimethyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane) is prepared according to J.Amer.Chem.Soc., (1990), 112, 8604. Bcyclam (1.00 g., 3.93 mmol) is dissolved in dry CH<sub>3</sub>CN (35 mL, distilled from CaH<sub>2</sub>). The solution is evacuated at 15 mm until the CH<sub>3</sub>CN begins to boil. The flask is then brought to atmospheric pressure with Ar. This degassing procedure is repeated 4 times. Mn(pyridine)<sub>2</sub>Cl<sub>2</sub> (1.12 g., 3.93 mmol), synthesized according to the literature procedure of J. Inorg. Nucl. Chem., (1974), 36, 1535, is added under Ar and the mixture is stirred overnight at room temperature. The reaction solution is filtered with a 0.2μ filter. The filtrate is evaporated. 1.35 g. of product is collected, 90% yield.

5 The bleach catalyst is typically used in a catalytically effective amount in the compositions and processes herein. By "catalytically effective amount" is meant an amount which is sufficient, under whatever comparative test conditions are employed, to enhance bleaching and removal of the stain or stains of interest from the target substrate. The test conditions will vary, depending on the type of washing appliance used and the habits of the user. Some users elect to use very hot water; others use warm or even cold water in laundering operations. Of course, the catalytic performance of the bleach catalyst will be affected by such considerations, and the levels of bleach catalyst used in fully-formulated  
10 detergent and bleach compositions can be appropriately adjusted. As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 1 ppm to about 200 ppm of the catalyst species in the wash liquor. To illustrate this point further, on the order of 3 micromolar manganese catalyst is effective at 40°C, pH 10 under European conditions using perborate and a peroxyacid bleach precursor. An increase in concentration of 3-5 fold may be required under U.S. conditions to achieve the same results.  
15 Therefore, the metal bleach catalyst are generally comprised in the detergent compositions of the present invention at a level of from 1ppb to 10%, preferably from about 0.1 ppm to about 1% most preferably from about 1 ppm to about 0.1% by weight of the composition.

25 More preferred metal bleach catalysts for the detergent compositions of the present invention is the cobalt catalysts  $\text{Co}[(\text{NH}_3)_n\text{M}_m\text{B}_b\text{T}_t\text{Q}_q\text{P}_p]\text{Y}_y$  described in US 5,798,326 (See supra); the cobalt catalyst  $[\text{Co}(\text{NH}_3)_5\text{M}]\text{T}_y$  described in US 5, 703,030 (See supra); the catalyst comprising a transition metal and a cross-bridged macropolycyclic ligant  $[\text{Mn}(\text{Bcyclam})\text{Cl}_2]$  and/or mixtures thereof.

30

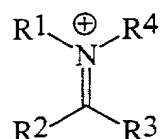
#### The bleach booster

35 The third bleach system that can be selected for the detergent compositions of the present invention, is a combination of a bleach booster including zwitterionic imines, anionic imine polyions having a net negative charge of from about -1 to about -3, and mixtures thereof; with a peroxygen source.

Suitable imine bleach boosters of the present invention include those of the general structure:

5

(I)

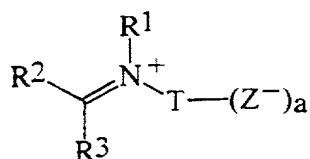


10

where  $\text{R}^1\text{-R}^4$  may be a hydrogen or an unsubstituted or substituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl and cycloalkyl radicals except that at least one of  $\text{R}^1\text{-R}^4$  contains an anionically charged moiety.

The preferred bleach boosters of the present invention include the anionically charged moiety bonded to the imine nitrogen and are represented by the formula:

(II)



15

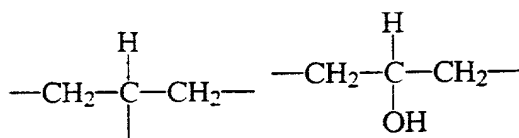
wherein:

$\text{R}^1 - \text{R}^3$  are moieties having a total charge of from about 0 to about -1;

20

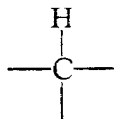
$\text{R}^1 - \text{R}^3$  may be a hydrogen or an unsubstituted or substituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl and cycloalkyl radicals;

T is selected from the group consisting of:  $-(\text{CH}_2)_b-$  wherein b is from about 1 to about 8,  $-(\text{CH}(\text{R}^5))-$  wherein  $\text{R}^5$  is  $\text{C}_1\text{-C}_8$  alkyl,  $-\text{CH}_2(\text{C}_6\text{H}_4)-$ ,



25

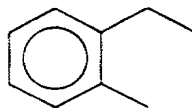
and  $-(\text{CH}_2)_d(\text{E})(\text{CH}_2)_f-$  wherein d is from 2 to 8, f is from 1 to 3 and E is  $-\text{C}(\text{O})\text{O}-$ ,  $-\text{C}(\text{O})\text{NR}^6$  or



- wherein  $R^6$  is H or  $C_1$ - $C_4$  alkyl.

- Z is covalently bonded to T and is selected from the group consisting of  $\text{CO}_2^-$ ,  $\text{SO}_3^-$  and  $\text{OSO}_3^-$  and a is at least 1. Accordingly, as Z is covalently bonded to T (when the total charge on  $R^1$ - $R^3$  is zero), the imine is either a zwitterion when a is 1 or a polyion having a net negative charge when a is greater than 1. Preferably, a is either 1 or 2 and the bleach booster is either a zwitterion or a polyion having a net charge of -1.
- In a more preferred embodiment, the bleach booster of the present invention is an aryliminium zwitterion, an aryliminium polyion having a net negative charge of about -1 to about -3 or mixtures thereof. In this preferred embodiment,  $R^1$  and  $R^2$  together form part of a common ring. In particular,  $R^1$  and  $R^2$  together may form one or more five-membered, six-membered or seven-membered rings. The most preferred aryliminiums are created from the non-charged moiety:

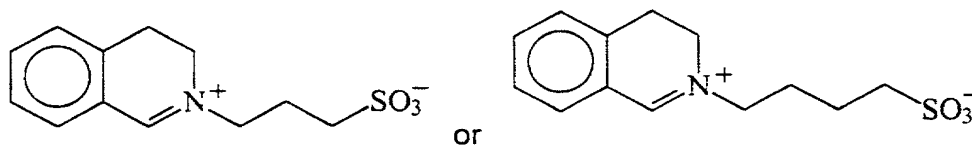
(III)



- Accordingly, the preferred aryliminium zwitterions involve  $R^1$  and  $R^2$  together forming the non-charged moiety (III) with T being selected from the group consisting of  $-(\text{CH}_2)_b-$  wherein b is from about 1 to about 6,  $-(\text{CH}(\text{R}^5))-$  wherein  $\text{R}^5$  is methyl, and  $-\text{CH}_2(\text{C}_6\text{H}_4)-$ , with a being 1 and Z being selected from  $\text{CO}_2^-$  and  $\text{SO}_3^-$ . More preferably, the aryliminium zwitterion of the present invention has  $R^1$  and  $R^2$  together forming the non-charged moiety (III) with T being  $-(\text{CH}_2)_b-$  or  $-\text{CH}_2(\text{C}_6\text{H}_4)-$ , with a being 1, Z being  $\text{SO}_3^-$  and b being from 2 to 4. The most preferred aryliminium zwitterions according to the present invention are represented by the formula:

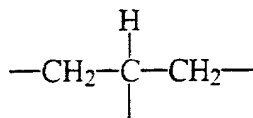
(IV)

(V)

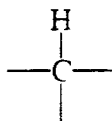


3-(3,4-dihydroisoquinolinium)propane sulfonate 4-(3,4-dihydroisoquinolinium)butane sulfonate, respectively.

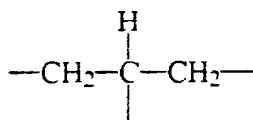
- 5 The preferred aryliminium polyions according to the present invention involve R<sup>1</sup> and R<sup>2</sup> together forming the non-charged moiety (III) with T being selected from:



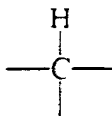
and  $-(\text{CH}_2)_d(\text{E})(\text{CH}_2)_f$  wherein d is from 2 to 8, f is from 1 to 3 and E is:



- 10 with a being at least 2 and Z being selected from  $\text{CO}_2^-$  and  $-\text{SO}_3^-$ . More preferably, the aryliminium polyion of the present invention has R<sup>1</sup> and R<sup>2</sup> together forming the non-charged moiety (III) with T being:



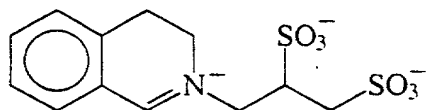
- 15 and  $-(\text{CH}_2)_d(\text{E})(\text{CH}_2)_f$  wherein d is from 2 to 6, f is 1 and E is:



with a being 2 and Z being  $-\text{SO}_3^-$ . The most preferred polyion according to the present invention is represented by the formula:

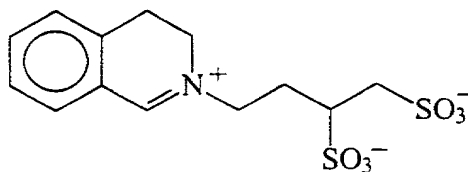
20

(VI)



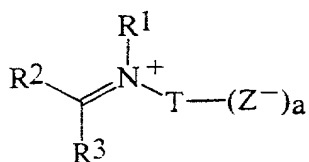
or

(VII)



- 25 Other suitable imines bleach boosters of the present invention comprise quaternary imine zwitterions represented by the formula:

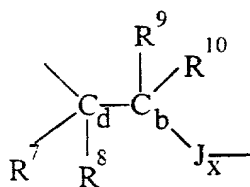
(II)



wherein:

- 5  $\text{R}^1 - \text{R}^3$  may be a hydrogen or an unsubstituted or substituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl and cycloalkyl radicals;

T is



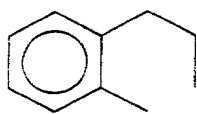
- 10 wherein x is equal to 0 or 1; J, when present, is selected from the group consisting of -CR<sup>11</sup>R<sup>12</sup>-, -CR<sup>11</sup>R<sup>12</sup>CR<sup>13</sup>R<sup>14</sup>-, and -CR<sup>11</sup>R<sup>12</sup>CR<sup>13</sup>R<sup>14</sup>CR<sup>15</sup>R<sup>16</sup>-; R<sup>7</sup>-R<sup>16</sup> are individually selected from the group consisting of H, linear or branched C<sub>1</sub>-C<sub>18</sub> substituted or unsubstituted alkyl, alkylene, oxyalkylene, aryl, substituted aryl, substituted arylcarbonyl groups, and amide groups; provided that at least one of R<sup>7</sup>-R<sup>8</sup> must be H or methyl, and that when neither R<sup>9</sup> nor R<sup>10</sup> is H, one of R<sup>7</sup>-R<sup>8</sup> must be H. Preferably, at least one of R<sup>9</sup> and R<sup>10</sup> must also be H. C<sub>b</sub> and C<sub>d</sub> are carbon atoms.

- 20 Z is covalently bonded to J<sub>x</sub> when x is 1 and to C<sub>b</sub> when x is 0 and is selected from the group consisting of -CO<sub>2</sub><sup>-</sup>, -SO<sub>2</sub><sup>-</sup>, -PO<sub>3</sub><sup>-</sup>, -OPO<sub>3</sub><sup>-</sup>, -SO<sub>3</sub><sup>-</sup> and -OSO<sub>3</sub><sup>-</sup> with -OSO<sub>3</sub><sup>-</sup> being preferred and a being 1. Accordingly, as Z is covalently bonded (when the total charge on R<sup>1</sup>-R<sup>3</sup> is zero), the quaternary imine is a zwitterion.

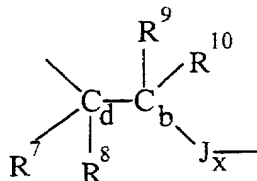
- 25 In a more preferred embodiment, the bleach booster of the present invention is an aryliminium zwitterion. In this preferred embodiment, R<sup>1</sup> and R<sup>2</sup> together form part of a common ring. In particular, R<sup>1</sup> and R<sup>2</sup> together may form one or more five-membered, six-membered or seven-membered rings. The most preferred aryliminiums are created from the non-charged moiety:

(III)

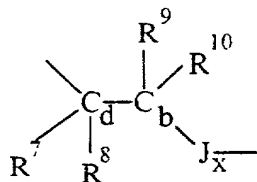




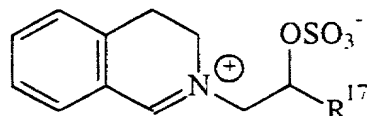
Accordingly, the preferred aryliminium zwitterions involve R<sup>1</sup> and R<sup>2</sup> together forming the non-charged moiety (III) with T being



- 5 with a being 1 and Z being selected from -OSO<sub>3</sub><sup>-</sup> and -SO<sub>3</sub><sup>-</sup>. More preferably, the aryliminium zwitterion of the present invention has R<sup>1</sup> and R<sup>2</sup> together forming the non-charged moiety (III) with T being:



- 10 with a being 1, Z being -OSO<sub>3</sub><sup>-</sup>. The most preferred aryliminium zwitterions according to the present invention are represented by the formula:



(IV)

- where R<sup>17</sup> is selected from the group consisting of H and linear or branched C<sub>1</sub>-C<sub>18</sub> substituted or unsubstituted alkyl, preferably C<sub>1</sub>-C<sub>14</sub> alkyl and even more preferably C<sub>8</sub>-C<sub>10</sub> linear alkyl chain.

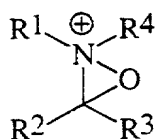
- Such bleach boosters can be prepared in accordance with the method described in the international co-pending application WO97/10323 internationally filed by The Procter & Gamble company on August 30, 1996 and especially with reference to examples I-III and/or the method described in the internationally co-pending application WO98/16614 filed by Procter & Gamble on August 28, 1997 and especially with reference to examples I-VIII.

- The bleach boosters of the present invention will be employed in conjunction with a peroxygen source in a bleaching composition. The peroxygen source is

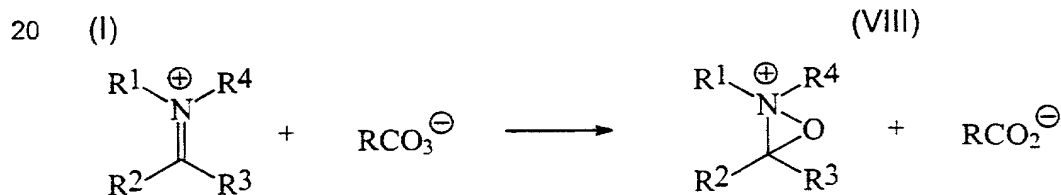
generally present in the detergent compositions of the present invention at a level of from 0.1% to 60% by weight of the composition, and preferably from 1% to 40% by weight of the composition. The bleach booster is generally present in the detergent compositions of the present invention at a level of from 0.01% to 10% by weight of the composition, and more preferably from 0.05% to 5% by weight of the composition.

The imine bleach booster of the present invention acts in conjunction with a peroxygen source to increase bleaching effectiveness. The bleach booster reacts with the peroxygen source to form a more active bleaching species, a oxaziridinium compound. The formed oxaziridinium compounds are either zwitterionic or polyionic with a net negative charge as was the imine bleach booster. The oxaziridinium compound has an increased activity at lower temperatures relative to the peroxygen compound. The oxaziridinium compound is represented by the formula:

(VIII)

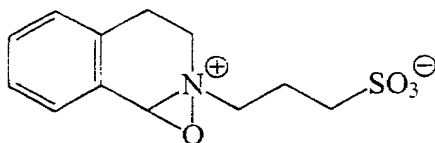


and can be produced from the imine of the present invention with the reaction:



Thus, the preferred bleach booster of the present invention represented by the formula (IV) produces the active oxaziridinium bleaching species represented by the formula:

(IX)



### The peroxygen Source

Peroxygen sources are well-known in the art and the peroxygen source employed in the present invention may comprise any of these well known sources, including peroxygen compounds as well as compounds which under consumer use conditions provide an effective amount of peroxygen in situ. The peroxygen source may include a hydrogen peroxide source, the in situ formation of a peracid anion through the reaction of a hydrogen peroxide source and a bleach activator, preformed peracid compounds or mixtures of suitable peroxygen sources. Such peroxygen source include for example, inorganic perhydrate bleaches or organic peroxyacids. In a preferred execution the bleaching system contains a hydrogen peroxide source and a peroxyacid bleach precursor compound. The production of the peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches. Of course, one of ordinary skill in the art will recognize that other sources of peroxygen may be employed without departing from the scope of the invention.

The preformed peracid compound as used herein is any convenient compound which under consumer use conditions provides an effective amount of peracid anion. Suitable non-limiting examples include percarboxylic acid and salts, percarbonic acids and salts, perimidic acids and salts, peroxymonosulfuric acids and salts, and mixtures thereof. Suitable examples of percarboxylic acids and salts include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent 4,634,551 to Burns et al, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Sources also include 6-nonylamino-6-oxoperoxyacaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al. Persulfate compounds such as for example OXONE, manufactured commercially by E.I. DuPont de

Nemours of Wilmington, DE can also be employed as a suitable source of peroxymonosulfuric acid.

A source of hydrogen peroxide as used herein is any convenient compound or mixture which under consumer use conditions provides an effective amount of hydrogen peroxide. Levels in general may vary widely and are typically from about 0.1% to about 60%, more typically from about 1% to about 40%, by weight of the bleaching compositions herein. The source of hydrogen peroxide used herein can be any convenient source, including hydrogen peroxide itself. For example, perborate, e.g., sodium perborate (any hydrate but preferably the mono- or tetra-hydrate), sodium carbonate peroxyhydrate or equivalent percarbonate salts, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, or sodium peroxide can be used herein. Mixtures of any convenient hydrogen peroxide sources can also be used.

#### Inorganic perhydrate bleaches

Inorganic perhydrate salts are a preferred source of hydrogen peroxide. These salts are normally incorporated in the form of the sodium salt at a level of from 1% to 95% by weight, more preferably from 10% to 90% by weight and most preferably from 20% to 80% by weight of the bleaching compositions. When incorporated in a bleaching composition which is comprised in a detergent composition in accordance with the present invention, the inorganic perhydrate salts are preferably present at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the detergent composition.

Examples of inorganic perhydrate salts include perborate, perphosphate, persulfate and persilicate salts. A preferred inorganic perhydrate salt is an alkali or alkaline earth metal percarbonate salt.

Sodium percarbonate, which is a preferred percarbonate salt for inclusion in bleach compositions in accordance with the invention, is an addition compound having a formula corresponding to  $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ , and is available commercially as a crystalline solid. The percarbonate is most preferably incorporated into such compositions in a coated form which provides in product stability. A preferred percarbonate bleach comprises dry particles having an

average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

10 Sodium perborate can be in the form of the monohydrate of nominal formula  $\text{NaBO}_2\text{H}_2\text{O}_2$  or the tetrahydrate  $\text{NaBO}_2\text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ .

The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilise a coated form of the material which provides better storage stability for the perhydrate salt in the granular product.

A suitable coating material providing in product stability comprises mixed salt of a water soluble alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interlox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1 : 200 to 1 : 4, more preferably from 1 : 99 to 1 : 9, and most preferably from 1 : 49 to 1 : 19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula  $\text{Na}_2\text{SO}_4 \cdot n \cdot \text{Na}_2\text{CO}_3$  wherein n is from 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5.

Other coatings which contain silicate (alone or with borate salts or boric acids or other inorganics), waxes, oils, fatty soaps can also be used advantageously within the present invention.

Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

35 Peroxyacid bleach precursor compound

Peroxyacid bleach precursors are preferably incorporated at a level of from 1% to 50% by weight, more preferably from 2% to 30% by weight, most preferably from 5% to 20% by weight of the bleaching compositions.

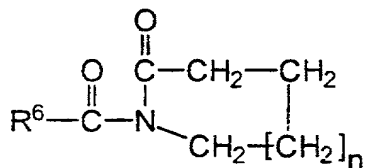
When incorporated in a bleaching composition which is comprised in a detergent composition in accordance with the invention, the peroxyacid bleach precursors are preferably present at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight and most preferably from 1.5% to 10% by weight of the detergent composition.

Suitable peroxyacid bleach precursors typically contain one or more N- or O- acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

#### N-acylated lactam precursor compound

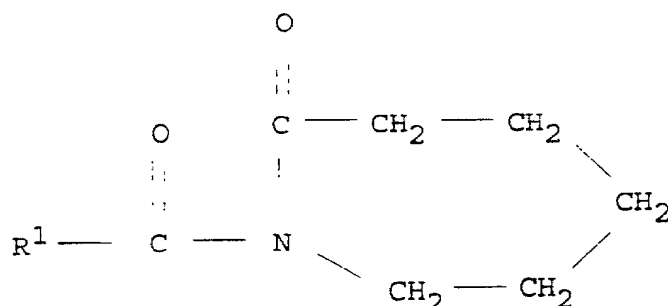
N-acylated precursor compounds of the lactam class are disclosed generally in GB-A-855735. Whilst the broadest aspect of the invention contemplates the use of any lactam useful as a peroxyacid precursor, preferred materials comprise the caprolactams and valerolactams.

Suitable N-acylated lactam precursors have the formula:



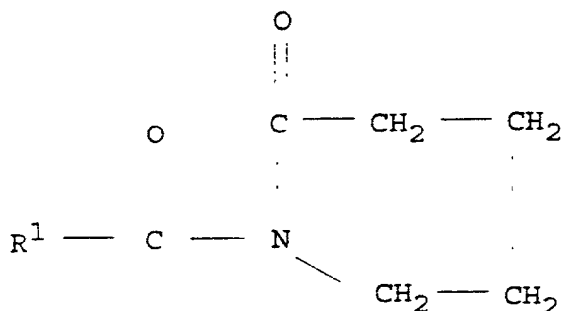
wherein n is from 0 to about 8, preferably from 0 to 2, and R<sup>6</sup> is H, an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbons, or a substituted phenyl group containing from 6 to 18 carbon atoms

Suitable caprolactam bleach precursors are of the formula:



wherein R<sup>1</sup> is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbon atoms, preferably from 6 to 12 carbon atoms, most preferably R<sup>1</sup> is phenyl.

Suitable valero lactams have the formula:



wherein R<sup>1</sup> is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbon atoms, preferably from 6 to 12 carbon atoms. In highly preferred embodiments, R<sup>1</sup> is selected from phenyl, heptyl, octyl, nonyl, 2,4,4-trimethylpentyl, decenyl and mixtures thereof.

The most preferred materials are those which are normally solid at <30°C, particularly the phenyl derivatives, i.e. benzoyl valerolactam, benzoyl caprolactam and their substituted benzoyl analogues such as chloro, amino alkyl, alkyl, aryl and alkoxy derivatives.

Caprolactam and valerolactam precursor materials wherein the R<sup>1</sup> moiety contains at least 6, preferably from 6 to 12, carbon atoms provide peroxyacids on perhydrolysis of a hydrophobic character which afford nucleophilic and body soil clean-up. Precursor compounds wherein R<sup>1</sup> comprises from 1 to 6 carbon

atoms provide hydrophilic bleaching species which are particularly efficient for bleaching beverage stains. Mixtures of 'hydrophobic' and 'hydrophilic' caprolactams and valero lactams, typically at weight ratios of 1:5 to 5:1, preferably 1:1, can be used herein for mixed stain removal benefits.

5

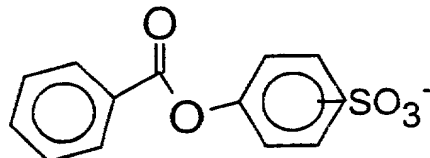
Highly preferred caprolactam and valerolactam precursors include benzoyl caprolactam, nonanoyl capro-lactam, benzoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl caprolactam, 3,5,5-trimethylhexanoyl valerolactam, octanoyl caprolactam, octanoyl valerolactam, decanoyl caprolactam, decanoyl valerolactam, undecenoyl caprolactam, undecenoyl valerolactam, (6-octanamidocaproyl)oxybenzene-sulfonate, (6-nonanamido-caproyl)oxybenzenesulfonate, (6-decanamidocaproyl)-oxybenzene-sulfonate, and mixtures thereof. Examples of highly preferred substituted benzoyl lactams include methylbenzoyl caprolactam, methylbenzoyl valerolactam, ethylbenzoyl caprolactam, ethylbenzoyl vaierolactam, propylbenzoyl caprolactam, propylbenzoyl valerolactam, isopropylbenzoyl caprolactam, isopropylbenzoyl valerolactam, butylbenzoyl caprolactam, butylbenzoyl valerolactam, tert-butylbenzoyl caprolactam, tert-butylbenzoyl valerolactam, pentylbenzoyl caprolactam, pentylbenzoyl valerolactam, hexylbenzoyl caprolactam, hexylbenzoyl valerolactam, ethoxybenzoyl caprolactam, ethoxybenzoyl valerolactam, propoxybenzoyl caprolactam, propoxybenzoyl valerolactam, isopropoxybenzoyl caprolactam, isopropoxybenzoyl valerolactam, butoxybenzoyl caprolactam, butoxybenzoyl valerolactam, tert-butoxybenzoyl caprolactam, tert-butoxybenzoyl valerolactam, pentoxybenzoyl caprolactam, pentoxybenzoyl valerolactam, hexoxybenzoyl caprolactam, hexoxybenzoyl valerolactam, 2,4,6-trichlorobenzoyl caprolactam, 2,4,6-trichlorobenzoyl valerolactam, pentafluorobenzoyl caprolactam, pentafluorobenzoyl valerolactam, dichlorobenzoyl caprolactam, dimethoxybenzoyl caprolactam, 4-chlorobenzoyl caprolactam, 2,4-dichlororbenzoyl caprolactam, terephthaloyl dicaprolactam, pentafluorobenzoyl caprolactam, pentafluorobenzoyl valerolactam, dichlorobenzoyl valerolactam, dimethoxybenzoyl valerolactam, 4-chlorobenzoyl valerolactam, 2,4-dichlororbenzoyl valerolactam, terephthaloyl divalerolactam, 4-nitrobenzoyl caprolactam, 4-nitrobenzoyl valerolactam, and mixtures thereof.

35 Perbenzoic acid precursor

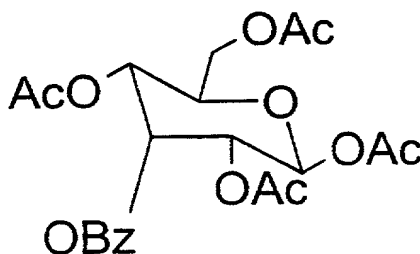


Essentially any perbenzoic acid precursors are suitable herein, including those of the N-acylated lactam class, which are preferred.

- 5 Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, including for example benzoyl oxybenzene sulfonate:



- 10 Also suitable are the benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents, including for example:

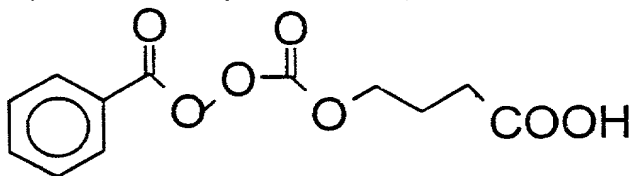


Ac = COCH<sub>3</sub>; Bz = Benzoyl

15

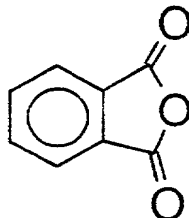
- Preferred perbenzoic acid precursor compounds of the imide type include N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole and other useful N-acyl group-  
20 containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Preferred perbenzoic acid precursors include the benzoyl diacyl peroxides, the benzoyl tetraacyl peroxides, and the compound having the formula:



25

Phthalic anhydride is another suitable perbenzoic acid precursor compound herein:



5

#### Perbenzoic acid derivative precursors

Suitable perbenzoic acid derivative precursors include any of the herein disclosed perbenzoic precursors in which the perbenzoic group is substituted by essentially any functional group including alkyl groups.

10

#### Cationic peroxyacid precursors

Cationic peroxyacid precursor compounds are also suitable herein. Typically such cationic peroxyacid precursors are formed by substituting the peroxyacid part with an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group.

15

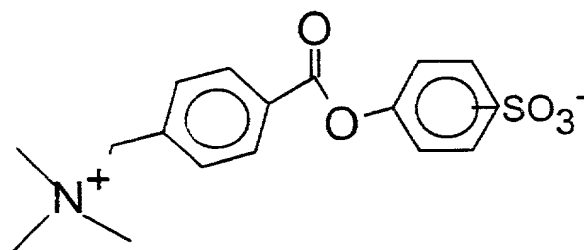
Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

20

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

25 Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides.

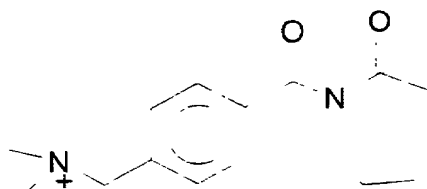
30 A preferred cationically substituted benzoyl oxybenzene sulfonate is the 4-(trimethyl ammonium) methyl derivative of benzoyl oxybenzene sulfonate:



A preferred cationically substituted alkyl oxybenzene sulfonate is the methyl ammonium derivative of 2,3,3-tri-methyl hexanoyloxybenzene sulfonate.

5

Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams, particularly trimethyl ammonium methylene benzoyl caprolactam:



10

Another preferred cationic peroxyacid precursor is 2-(N,N,N-trimethyl ammonium) ethyl sodium 4-sulphophenyl carbonate chloride.

#### 15 Alkyl fatty peroxyacid bleach precursors

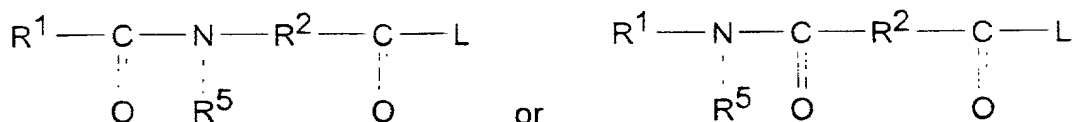
Alkyl fatty peroxyacid bleach precursors form alkyl fatty peroxyacids on perhydrolysis. Preferred precursors of this type give rise to peracetic acid on perhydrolysis.

20 Preferred alkyl fatty peroxyacid precursor compounds of the imide type include the N-,N,N<sup>1</sup>N<sup>1</sup> tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

25

#### Amide substituted peroxyacid bleach precursors

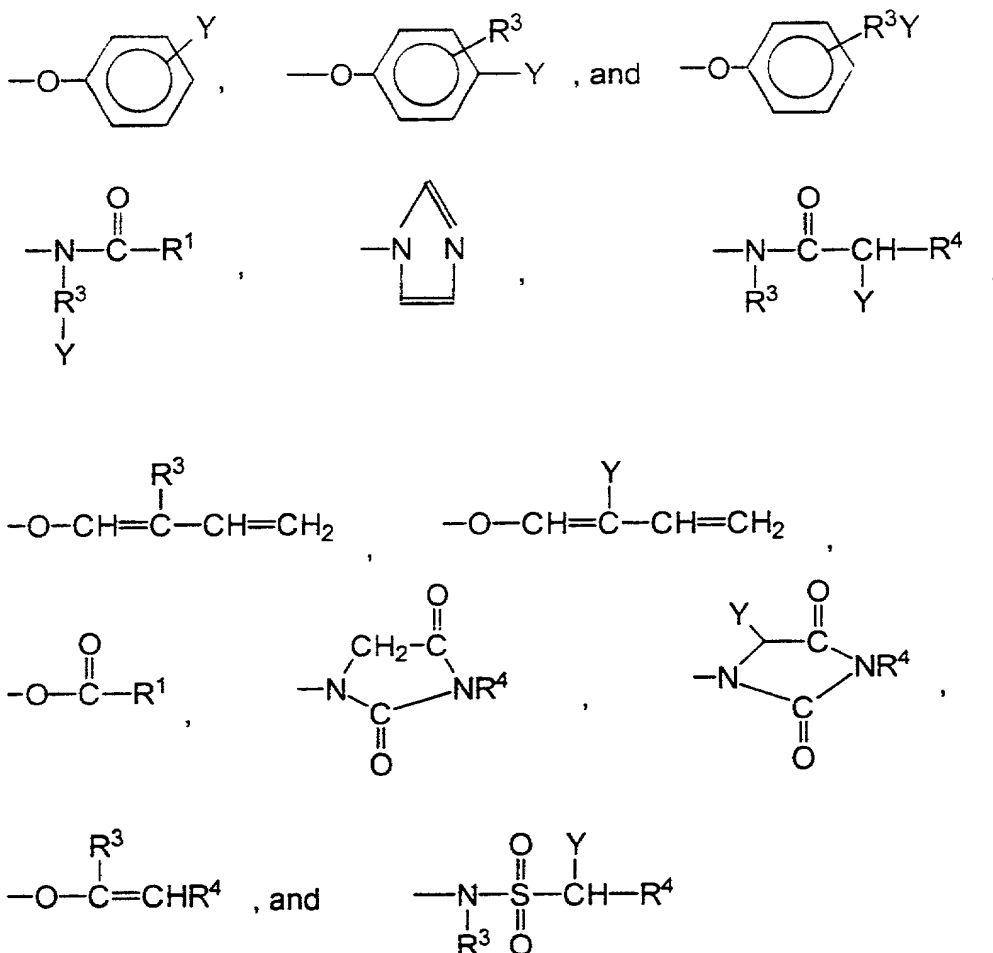
Another preferred class of peroxyacid bleach activator compounds are the amide substituted compounds of the following general formulae:



wherein R<sup>1</sup> is an alkyl or aryl group with from 1 to 14 carbon atoms, R<sup>2</sup> is an  
 5 alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms,  
 and R<sup>5</sup> is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms  
 and L can be essentially any leaving group. R<sup>1</sup> preferably contains from 6 to 12  
 carbon atoms. R<sup>2</sup> preferably contains from 4 to 8 carbon atoms. R<sup>1</sup> may be  
 10 straight chain or branched alkyl containing branching, substitution, or both and  
 may be sourced from either synthetic sources or natural sources including for  
 example, tallow fat. Analogous structural variations are permissible for R<sup>2</sup>. The  
 substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical  
 substituent groups or organic compounds. R<sup>5</sup> is preferably H or methyl. R<sup>1</sup> and  
 15 R<sup>5</sup> should not contain more than 18 carbon atoms in total. L may be selected  
 from any of the leaving groups described hereinbefore for the analogues having  
 R<sup>1</sup> as an aryl or alkaryl group. Amide substituted bleach activator compounds of  
 this type are described in EP-A-0170386.

The L group must be sufficiently reactive for the reaction to occur within the  
 20 optimum time frame (e.g., a wash cycle). However, if L is too reactive, this  
 activator will be difficult to stabilize for use in a bleaching composition. These  
 characteristics are generally paralleled by the pKa of the conjugate acid of the  
 leaving group, although exceptions to this convention are known. Ordinarily,  
 leaving groups that exhibit such behaviour are those in which their conjugate acid  
 25 has a pKa in the range of from 4 to 13, preferably from 6 to 11 and most  
 preferably from 8 to 11.

Preferred bleach precursors are those wherein R<sup>1</sup>, R<sup>2</sup> and R<sup>5</sup> are as defined for  
 the amide substituted compounds and L is selected from the group consisting of:



5

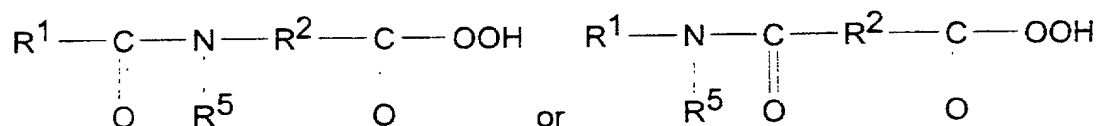
and mixtures thereof, wherein  $\text{R}^1$  is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms,  $\text{R}^3$  is an alkyl chain containing from 1 to 8 carbon atoms,  $\text{R}^4$  is H or  $\text{R}^3$ , and Y is H or a solubilizing group.

- 10 The preferred solubilizing groups are  $\text{---SO}_3^-\text{M}^+$ ,  $\text{---CO}_2^-\text{M}^+$ ,  $\text{---SO}_4^-\text{M}^+$ ,  $\text{---N}^+(\text{R}^3)_4\text{X}^-$  and  $\text{O}=\text{N}(\text{R}^3)_3$  and most preferably  $\text{---SO}_3^-\text{M}^+$  and  $\text{---CO}_2^-\text{M}^+$  wherein  $\text{R}^3$  is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion. It should be noted that bleach activators with a leaving group that does not contain a solubilizing groups should be well dispersed in the bleaching solution in order to assist in their dissolution.
- 15

20 Organic peroxyacids

The compositions may contain as components of the bleaching system organic peroxyacids, typically at a level of from 2% to 30% by weight, more preferably from 5% to 20% by weight of the bleaching composition. When the bleaching compositions are comprised in a detergent composition in accordance with the present invention, the organic peroxyacid is preferably present at a level of from 1% to 15% by weight and more preferably from 1% to 10% by weight of the detergent composition.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein R<sup>1</sup> is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R<sup>2</sup> is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R<sup>5</sup> is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. R<sup>1</sup> preferably contains from 6 to 12 carbon atoms. R<sup>2</sup> preferably contains from 4 to 8 carbon atoms. R<sup>1</sup> may be straight chain or branched alkyl, substituted aryl or alkaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R<sup>2</sup>. The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R<sup>5</sup> is preferably H or methyl. R<sup>1</sup> and R<sup>5</sup> should not contain more than 18 carbon atoms in total. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diperoxydodecanedioc acid, diperoxytetradecanedioc acid, diperoxyhexadecanedioc acid, mono- and diperazelaic acid, mono- and diperbrassylic acid.

Also suitable is the nonanoyl-oxybenzene-sulfonate (NOBS, described in US 4,412,934). Useful bleaching agents, including peroxyacids and bleaching systems comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention are described in our co-

pending applications USSN 08/136,626, PCT/US95/07823, WO95/27772, WO95/27773, WO95/27774 and WO95/27775.

5 The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

### 10 Detergent components

15 The detergent compositions of the invention will preferably comprise further additional detergent components. The precise nature of these additional component, and levels of incorporation thereof will depend on the physical form of the composition, and the nature of the cleaning operation for which it is to be used.

20 The detergent compositions according to the invention can be liquid, paste, gels, bars, tablets, spray, foam, powder or granular. Granular compositions can also be in "compact" form and the liquid compositions can also be in a "concentrated" form. Tablet compositions can be in single phase or multiple phase form.

25 It has been surprisingly found that the cleaning benefits of pectate lyase enzymes can be optimised and maximised with a time controlled release technology. In particular, the time controlled technology is a tablet wherein the pectate lyase is separated from the inhibiting / deactivating other detergent ingredients in a different product phase having a different solubility in the wash. It has been surprisingly found that optimal performance efficiency of the pectate  
30 lyase enzyme can be achieved when said enzyme is incorporated into a tablet and such system delivers significant soil and stain cleaning benefits. It has further been found that such time controlled release technology allows a broader range of Pectate Lyases to be used, including those that show a high degree of instability in standard detergent matrices. Indeed, the pectate lyase and buffer  
35 materials can preferably be incorporated into the rapid dissolving portion of the tablet. Without wishing to be bound by theory, it is believed that the pectate lyase

is released earlier than the inhibiting / deactivating other detergent ingredients and that optimum pectate lyase activity is obtained at the beginning of the wash under buffered conditions, allowing the formulation in detergent of pectate lyases in the full range of available pectate lyases.

5

Suitable tablets are detergent tablets which are not only sufficiently robust to withstand handling and transportation, but also at least a portion of which dissolves rapidly in the wash water providing rapid delivery of the pectate lyase enzyme. It is preferred that at least one phase of the tablet dissolves in the wash  
10 water within the first ten minutes, preferably five minutes, more preferably four minutes of the wash cycle of an automatic dishwashing or laundry washing machine. Preferably the washing machine is either an automatic dishwashing or laundry washing machine. The time within which the multi-phase tablet or a phase thereof or a detergent active component dissolves is determined  
15 according to DIN 44990 using a dishwashing machine available from Bosch on the normal 65°C washing program with water hardness at 18°H using a minimum of six replicates or a sufficient number to ensure reproducibility.

In a first embodiment, the present invention relates to laundry detergent  
20 compositions comprising a pectate lyase and a selected bleach system (Examples 1-16). In a second embodiment, the present invention relates to dishwashing detergent compositions comprising a pectate lyase, a peroxygen source, and a bleach booster (Examples 17-27).

25 The bleaching composition of the present invention may be advantageously employed in laundry applications, hard surface cleaning, automatic dishwashing applications, as well as cosmetic applications such as dentures, teeth, hair and skin. However, due to the unique advantages of both increased effectiveness in lower temperature solutions and the superior color-safety profile, the bleach  
30 boosters of the present invention are ideally suited for laundry applications such as the bleaching of fabrics through the use of bleach containing detergents or laundry bleach additives. Furthermore, the bleach boosters of the present invention may be employed in both granular and liquid compositions.

35 The compositions of the invention may for example, be formulated as hand dishwashing compositions, hand and machine laundry detergent compositions



including laundry additive compositions and compositions suitable for use in the soaking and/or pretreatment of stained fabrics and compositions for use in general household hard surface cleaning operations. When formulated as compositions for use in manual dishwashing methods the compositions of the invention preferably contain a surfactant and preferably other detergent compounds selected from organic polymeric compounds, suds enhancing agents, group II metal ions, solvents, hydrotropes and additional enzymes.

When formulated as compositions suitable for use in a laundry machine washing method, the compositions of the invention preferably contain both a surfactant and a builder compound and additionally one or more detergent components preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors. Laundry compositions can also contain softening agents, as additional detergent components. Such compositions containing a pectate lyase, a peroxygen source and a bleach booster can provide fabric cleaning, stain removal, and color appearance when formulated as laundry detergent compositions.

When formulated as compositions suitable for use in a machine dish wash method, the compositions of the invention preferably contain a low foaming nonionic surfactant, a builder system, and one or more components preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors.

The compositions of the invention can also be used as detergent additive products in solid or liquid form. Such additive products are intended to supplement or boost the performance of conventional detergent compositions and can be added at any stage of the cleaning process.

If needed the density of the laundry detergent compositions herein ranges from 400 to 1200 g/litre, preferably 500 to 950 g/litre of composition measured at 20°C.

The "compact" form of the compositions herein is best reflected by density and, in terms of composition, by the amount of inorganic filler salt; inorganic filler salts

are conventional ingredients of detergent compositions in powder form; in conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% by weight of the total composition. In the compact compositions, the filler salt is present in amounts not exceeding 15% of the total composition, preferably not exceeding 10%, most preferably not exceeding 5% by weight of the composition. The inorganic filler salts, such as meant in the present compositions are selected from the alkali and alkaline-earth-metal salts of sulphates and chlorides. A preferred filler salt is sodium sulphate.

Liquid detergent compositions according to the present invention can also be in a "concentrated form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents. Typically the water content of the concentrated liquid detergent is preferably less than 40%, more preferably less than 30%, most preferably less than 20% by weight of the detergent composition.

Suitable detergent compounds for use herein are selected from the group consisting of the below described compounds.

#### **Surfactant system**

Preferably, the detergent compositions of the present invention will comprise a surfactant system wherein the surfactant can be selected from cationic, nonionic and/or conventional anionic and/or mixtures thereof. Also suitable are ampholytic and/or zwitterionic and/or semi-polar surfactants.

The surfactant system is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation are 1% to 35% by weight, most preferably from 1% to 30% by weight of laundry detergent compositions in accord with the invention.

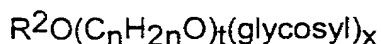
The surfactant is preferably formulated to be compatible with enzyme components present in the composition. In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of any enzyme in these compositions.

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal<sup>TM</sup> CO-630, marketed by the GAF Corporation; and Triton<sup>TM</sup> X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type include Tergitol<sup>TM</sup> 15-S-9 (the condensation product of C<sub>11</sub>-C<sub>15</sub> linear alcohol with 9 moles ethylene oxide), Tergitol<sup>TM</sup> 24-L-6 NMW (the condensation product of C<sub>12</sub>-C<sub>14</sub> primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol<sup>TM</sup> 45-9 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 9 moles of ethylene oxide), Neodol<sup>TM</sup> 23-3 (the condensation product of C<sub>12</sub>-C<sub>13</sub> linear alcohol with 3.0 moles of ethylene oxide), Neodol<sup>TM</sup> 45-7 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 7 moles of ethylene oxide), Neodol<sup>TM</sup> 45-5 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company,

Kyro<sup>TM</sup> EOB (the condensation product of C<sub>13</sub>-C<sub>15</sub> alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O3O or O5O (the condensation product of C<sub>12</sub>-C<sub>14</sub> alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products  
5 is from 8-11 and most preferred from 8-10.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from  
10 about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing  
15 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the  
20 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units. The preferred alkylpolyglycosides have the formula



wherein R<sup>2</sup> is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups  
25 contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To  
30 prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

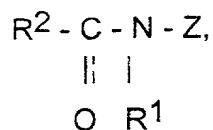
35

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Plurafac<sup>TM</sup> LF404 and Pluronic<sup>TM</sup> surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic<sup>TM</sup> compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C<sub>8</sub>-C<sub>14</sub> alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C<sub>8</sub>-C<sub>18</sub> alcohol ethoxylates (preferably C<sub>10</sub> avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

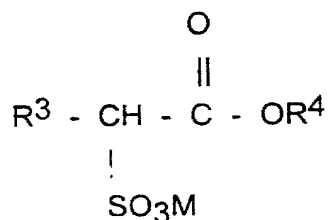
Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula.



- 5 wherein R<sup>1</sup> is H, or R<sup>1</sup> is C<sub>1-4</sub> hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R<sup>2</sup> is C<sub>5-31</sub> hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative thereof. Preferably, R<sup>1</sup> is methyl, R<sup>2</sup> is a straight C<sub>11-15</sub> alkyl or C<sub>16-18</sub> alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

15 Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C<sub>8</sub>-C<sub>20</sub> carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO<sub>3</sub> according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

20 The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula:



- 25 wherein R<sup>3</sup> is a C<sub>8</sub>-C<sub>20</sub> hydrocarbyl, preferably an alkyl, or combination thereof, R<sup>4</sup> is a C<sub>1</sub>-C<sub>6</sub> hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R<sup>3</sup> is C<sub>10</sub>-C<sub>16</sub> alkyl, and R<sup>4</sup> is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R<sup>3</sup> is C<sub>10</sub>-C<sub>16</sub> alkyl.

- 35 Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula ROSO<sub>3</sub>M wherein R preferably is a

C<sub>10</sub>-C<sub>24</sub> hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C<sub>10</sub>-C<sub>20</sub> alkyl component, more preferably a C<sub>12</sub>-C<sub>18</sub> alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl- ammonium cations and quaternary ammonium cations such as tetramethyl- ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C<sub>12</sub>-C<sub>16</sub> are preferred for lower wash temperatures (e.g. below about 50°C) and C<sub>16</sub>-18 alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for deterative purposes can also be included in the detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C<sub>8</sub>-C<sub>22</sub> primary or secondary alkanesulfonates, C<sub>8</sub>-C<sub>24</sub> olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C<sub>8</sub>-C<sub>24</sub> alkylpolyglycoethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C<sub>12</sub>-C<sub>18</sub> monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C<sub>6</sub>-C<sub>12</sub> diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula  $RO(CH_2CH_2O)_k-CH_2COO-M^+$  wherein R is a C<sub>8</sub>-C<sub>22</sub> alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to

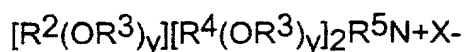
Laughlin. et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.

Highly preferred anionic surfactants include alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula  $RO(A)_mSO_3M$  wherein R is an unsubstituted  $C_{10}$ - $C_{24}$  alkyl or hydroxyalkyl group having a  $C_{10}$ - $C_{24}$  alkyl component, preferably a  $C_{12}$ - $C_{20}$  alkyl or hydroxyalkyl, more preferably  $C_{12}$ - $C_{18}$  alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are  $C_{12}$ - $C_{18}$  alkyl polyethoxylate (1.0) sulfate ( $C_{12}$ - $C_{18}E(1.0)M$ ),  $C_{12}$ - $C_{18}$  alkyl polyethoxylate (2.25) sulfate ( $C_{12}$ - $C_{18}E(2.25)M$ ),  $C_{12}$ - $C_{18}$  alkyl polyethoxylate (3.0) sulfate ( $C_{12}$ - $C_{18}E(3.0)M$ ), and  $C_{12}$ - $C_{18}$  alkyl polyethoxylate (4.0) sulfate ( $C_{12}$ - $C_{18}E(4.0)M$ ), wherein M is conveniently selected from sodium and potassium.

The detergent compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

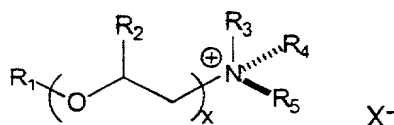
Cationic deterative surfactants suitable for use in the detergent compositions of the present invention are those having one long-chain hydrocarbonyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula :





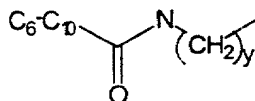
wherein  $R^2$  is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each  $R^3$  is selected from the group consisting of  $-CH_2CH_2-$ ,  $-CH_2CH(CH_3)-$ ,  $-CH_2CH(CH_2OH)-$ ,  $-CH_2CH_2CH_2-$ , and mixtures thereof; each  $R^4$  is selected from the group consisting of  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxyalkyl, benzyl ring structures formed by joining the two  $R^4$  groups,  $-CH_2CHOH-CHOHCOR^6CHOHCH_2OH$  wherein  $R^6$  is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when  $y$  is not 0;  $R^5$  is the same as  $R^4$  or is an alkyl chain wherein the total number of carbon atoms of  $R^2$  plus  $R^5$  is not more than about 18; each  $y$  is from 0 to about 10 and the sum of the  $y$  values is from 0 to about 15; and  $X$  is any compatible anion.

Quaternary ammonium surfactant suitable for the present invention has the formula (I):



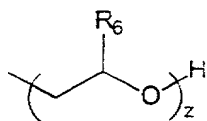
Formula I

whereby  $R_1$  is a short chainlength alkyl ( $C_6$ - $C_{10}$ ) or alkylamidoalkyl of the formula (II):



Formula II

$y$  is 2-4, preferably 3.  
 whereby  $R_2$  is H or a  $C_1$ - $C_3$  alkyl,  
 whereby  $x$  is 0-4, preferably 0-2, most preferably 0,  
 whereby  $R_3$ ,  $R_4$  and  $R_5$  are either the same or different and can be either a short chain alkyl ( $C_1$ - $C_3$ ) or alkoxylated alkyl of the formula III,  
 whereby  $X^-$  is a counterion, preferably a halide, e.g. chloride or methylsulfate.



Formula III

R<sub>6</sub> is C<sub>1</sub>-C<sub>4</sub> and z is 1 or 2.

- 5 Preferred quat ammonium surfactants are those as defined in formula I whereby R<sub>1</sub> is C<sub>8</sub>, C<sub>10</sub> or mixtures thereof, x=0, R<sub>3</sub>, R<sub>4</sub> = CH<sub>3</sub> and R<sub>5</sub> = CH<sub>2</sub>CH<sub>2</sub>OH.

- 10 Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :  
R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>N<sup>+</sup>X<sup>-</sup> (i)

- 15 wherein R<sub>1</sub> is C<sub>8</sub>-C<sub>16</sub> alkyl, each of R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> is independently C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> hydroxy alkyl, benzyl, and -(C<sub>2</sub>H<sub>4</sub>)<sub>x</sub>H where x has a value from 2 to 5, and X is an anion. Not more than one of R<sub>2</sub>, R<sub>3</sub> or R<sub>4</sub> should be benzyl.

- The preferred alkyl chain length for R<sub>1</sub> is C<sub>12</sub>-C<sub>15</sub> particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R<sub>2</sub>R<sub>3</sub> and R<sub>4</sub> are methyl and hydroxyethyl groups and the anion X  
20 may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

- coconut trimethyl ammonium chloride or bromide;  
coconut methyl dihydroxyethyl ammonium chloride or bromide;  
25 decyl triethyl ammonium chloride;  
decyl dimethyl hydroxyethyl ammonium chloride or bromide;  
C<sub>12</sub>-15 dimethyl hydroxyethyl ammonium chloride or bromide;  
coconut dimethyl hydroxyethyl ammonium chloride or bromide;  
myristyl trimethyl ammonium methyl sulphate;  
30 lauryl dimethyl benzyl ammonium chloride or bromide;  
lauryl dimethyl (ethenoxy)<sub>4</sub> ammonium chloride or bromide;  
choline esters (compounds of formula (i) wherein R<sub>1</sub> is

- 35 CH<sub>2</sub>-CH<sub>2</sub>-O-C-C<sub>12-14</sub> alkyl and R<sub>2</sub>R<sub>3</sub>R<sub>4</sub> are methyl).



di-alkyl imidazolines [compounds of formula (i)].

- 5 Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

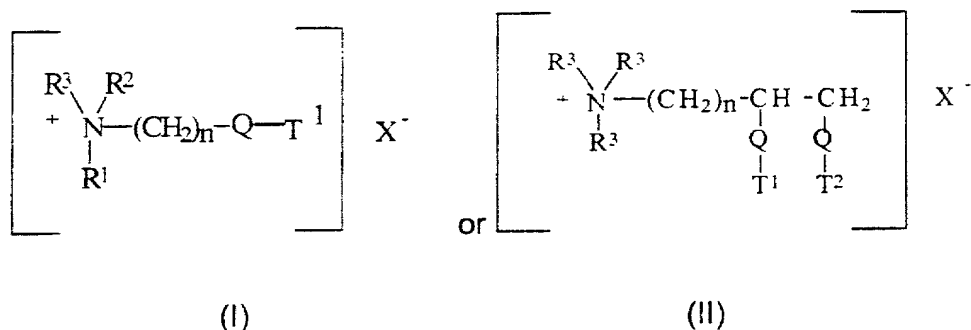
10 Typical cationic fabric softening components include the water-insoluble quaternary-ammonium fabric softening actives or their corresponding amine precursor, the most commonly used having been di-long alkyl chain ammonium chloride or methyl sulfate.

Preferred cationic softeners among these include the following:

- 1) ditallow dimethylammonium chloride (DTDMAC);
- 15 2) dihydrogenated tallow dimethylammonium chloride;
- 3) dihydrogenated tallow dimethylammonium methylsulfate;
- 4) distearyl dimethylammonium chloride;
- 5) dioleyl dimethylammonium chloride;
- 6) dipalmityl hydroxyethyl methylammonium chloride;
- 20 7) stearyl benzyl dimethylammonium chloride;
- 8) tallow trimethylammonium chloride;
- 9) hydrogenated tallow trimethylammonium chloride;
- 10) C<sub>12-14</sub> alkyl hydroxyethyl dimethylammonium chloride;
- 11) C<sub>12-18</sub> alkyl dihydroxyethyl methylammonium chloride;
- 25 12) di(stearoyloxyethyl) dimethylammonium chloride (DSOEDMAC);
- 13) di(tallow-oxy-ethyl) dimethylammonium chloride;
- 14) ditallow imidazolinium methylsulfate;
- 15) 1-(2-tallowylamidoethyl)-2-tallowyl imidazolinium methylsulfate.

30 Biodegradable quaternary ammonium compounds have been presented as alternatives to the traditionally used di-long alkyl chain ammonium chlorides and methyl sulfates. Such quaternary ammonium compounds contain long chain alk(en)yl groups interrupted by functional groups such as carboxy groups. Said materials and fabric softening compositions containing them are disclosed in  
35 numerous publications such as EP-A-0,040,562, and EP-A-0,239,910.

The quaternary ammonium compounds and amine precursors herein have the formula (I) or (II), below :



wherein Q is selected from -O-C(O)-, -C(O)-O-, -O-C(O)-O-, -NR<sup>4</sup>-C(O)-, -C(O)-NR<sup>4</sup>-;

10  $R^1$  is  $(CH_2)_n-Q-T^2$  or  $T^3$ ;

$R^2$  is  $(CH_2)_m-Q-T^4$  or  $T^5$  or  $R^3$ ;

R<sup>3</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl or H;

R<sup>4</sup> is H or C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl;

T<sup>1</sup>, T<sup>2</sup>, T<sup>3</sup>, T<sup>4</sup>, T<sup>5</sup> are independently C<sub>11</sub>-C<sub>22</sub> alkyl or alkenyl;

15      $n$  and  $m$  are integers from 1 to 4; and

X<sup>-</sup> is a softener-compatible anion. Non-limiting examples of softener-compatible anions include chloride or methyl sulfate.

The alkyl, or alkenyl, chain T<sup>1</sup>, T<sup>2</sup>, T<sup>3</sup>, T<sup>4</sup>, T<sup>5</sup> must contain at least 11 carbon atoms, preferably at least 16 carbon atoms. The chain may be straight or branched. Tallow is a convenient and inexpensive source of long chain alkyl and alkenyl material. The compounds wherein T<sup>1</sup>, T<sup>2</sup>, T<sup>3</sup>, T<sup>4</sup>, T<sup>5</sup> represents the mixture of long chain materials typical for tallow are particularly preferred.

25 Specific examples of quaternary ammonium compounds suitable for use in the aqueous fabric softening compositions herein include :

- 1) N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
- 2) N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;
- 30 3) N,N-di(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 4) N,N-di(2-tallowyl-oxy-ethylcarbonyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;

- 5) N-(2-tallowyl-oxy-2-ethyl)-N-(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
  - 6) N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
  - 7) N-(2-tallowyl-oxy-2-oxo-ethyl)-N-(tallowyl-N,N-dimethyl-ammonium chloride; and
  - 8) 1,2-ditallowyl-oxy-3-trimethylammoniopropane chloride;
- and mixtures of any of the above materials.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

Zwitterionic surfactants are also suitable for use in detergent compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



wherein  $R^3$  is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms;  $R^4$  is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof;  $x$  is from 0 to about 3; and each  $R^5$  is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The  $R^5$  groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include  $C_{10}$ - $C_{18}$  alkyl dimethyl amine oxides and  $C_8$ - $C_{12}$  alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

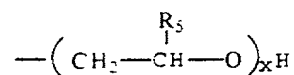
The detergent composition of the present invention may further comprise a cosurfactant selected from the group of primary or tertiary amines.

Suitable primary amines for use herein include amines according to the formula  $R_1NH_2$  wherein  $R_1$  is a  $C_6$ - $C_{12}$ , preferably  $C_6$ - $C_{10}$  alkyl chain or  $R_4X(CH_2)_n$ ,  $X$  is -O-, -C(O)NH- or -NH-,  $R_4$  is a  $C_6$ - $C_{12}$  alkyl chain  $n$  is between 1 to 5,

preferably 3. R<sub>1</sub> alkyl chains may be straight or branched and may be interrupted with up to 12, preferably less than 5 ethylene oxide moieties.

Preferred amines according to the formula herein above are n-alkyl amines. Suitable amines for use herein may be selected from 1-hexylamine, 1-octylamine, 1-decylamine and laurylamine. Other preferred primary amines include C8-C10 oxypropylamine, octyloxypropylamine, 2-ethylhexyl-oxypropylamine, lauryl amido propylamine and amido propylamine.

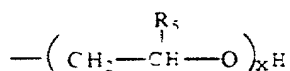
Suitable tertiary amines for use herein include tertiary amines having the formula R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>N wherein R<sub>1</sub> and R<sub>2</sub> are C<sub>1</sub>-C<sub>8</sub> alkyl chains or



R<sub>3</sub> is either a C<sub>6</sub>-C<sub>12</sub>, preferably C<sub>6</sub>-C<sub>10</sub> alkyl chain, or R<sub>3</sub> is R<sub>4</sub>X(CH<sub>2</sub>)<sub>n</sub>, whereby X is -O-, -C(O)NH- or -NH-, R<sub>4</sub> is a C<sub>4</sub>-C<sub>12</sub>, n is between 1 to 5, preferably 2-3. R<sub>5</sub> is H or C<sub>1</sub>-C<sub>2</sub> alkyl and x is between 1 to 6.

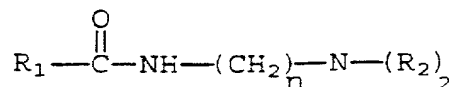
R<sub>3</sub> and R<sub>4</sub> may be linear or branched; R<sub>3</sub> alkyl chains may be interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

Preferred tertiary amines are R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>N where R<sub>1</sub> is a C<sub>6</sub>-C<sub>12</sub> alkyl chain, R<sub>2</sub> and R<sub>3</sub> are C<sub>1</sub>-C<sub>3</sub> alkyl or



where R<sub>5</sub> is H or CH<sub>3</sub> and x = 1-2.

Also preferred are the amidoamines of the formula:



wherein R<sub>1</sub> is C<sub>6</sub>-C<sub>12</sub> alkyl; n is 2-4, preferably n is 3; R<sub>2</sub> and R<sub>3</sub> is C<sub>1</sub>-C<sub>4</sub>

Most preferred amines of the present invention include 1-octylamine, 1-hexylamine, 1-decylamine, 1-dodecylamine, C8-10oxypropylamine, N coco 1-3diaminopropane, coconutalkyldimethylamine, lauryldimethylamine, lauryl bis(hydroxyethyl)amine, coco bis(hydroxyethyl)amine, lauryl amine 2 moles

propoxylated, octyl amine 2 moles propoxylated, lauryl amidopropyl-dimethylamine, C8-10 amidopropyldimethylamine and C10 amidopropyl-dimethylamine.

The most preferred amines for use in the compositions herein are 1-hexylamine,  
5 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecyldimethylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

### 10 ***Bleaching agent***

The detergent compositions of the present invention can in addition to the selected bleach system of the [present invention, further comprise another bleaching agent.

15 Bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added  
20 at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc  
25 and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are  
30 described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.

### 35 ***Builder system***



- The detergent compositions of the present invention can further comprise a builder. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates, alkyl- or alkenyl-succinic acid and fatty acids, materials such as ethylenediamine tetraacetate, diethylene triamine pentamethyleneacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Phosphate builders can also be used herein.
- 5 Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B, HS or MAP. Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate
- 15 ( $\text{Na}_2\text{Si}_2\text{O}_5$ ). Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy)
- 20 diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offeniegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates
- 25 described in British Patent No. 1,387,447.
- 30 Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S.
- 35 Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British

Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

5 Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydro-furan - cis, cis, cis-tetracarboxylates, 2,5-tetrahydro-furan -cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane -hexacarboxylates and and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic poly-carboxylates include mellitic acid, pyromellitic acid and  
10 the phthalic acid derivatives disclosed in British Patent No. 1,425,343. Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

15 Preferred builder systems for use in the present compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid. Other preferred builder systems include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid. Preferred builder systems for use in liquid  
20 detergent compositions of the present invention are soaps and polycarboxylates.

Other builder materials that can form part of the builder system for use in granular compositions include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic  
25 phosphonates, amino polyalkylene phosphonates and amino polycarboxylates. Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts  
30 are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

35 Detergency builder salts are normally included in amounts of from 5% to 80% by weight of the composition preferably from 10% to 70% and most usually from 30% to 60% by weight.

### ***Conventional detergent enzymes***

- 5 The detergent compositions can in addition to the pectate lyase enzyme further comprise one or more enzymes which provide cleaning performance, fabric care and/or sanitisation benefits. Preferably the detergent compositions of the present invention will further comprise a pectin lyase.
- 10 Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases, phospholipases, esterases, cutinases, other pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxxygenases, ligninases, pullulanases, tannases, pentosanases, malanases,  $\beta$ -glucanases, arabinosidases,
- 15 hyaluronidase, chondroitinase, laccase or mixtures thereof. A preferred combination is a detergent composition having cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.
- 20 Each type of pectin degrading enzyme has a unique profile of substrate specificity, activity and stability under different hardness, pH, temperature, surfactant and other detergent ingredient matrix conditions. Pectin degrading enzymes are specifically directed to degrade pectin substances and in particular plant cell walls. In particular, pectate lyase enzymes are specifically directed to
- 25 pectic acid chains of plant cell walls such as low methoxy pectins while pectin lyase is more specifically directed towards esterified pectin chains such as high methoxyl pectins. Moreover, it has been found that pectate lyases are metal and especially calcium sensitive, whereas pectin lyases do not require metals for stabilisation and optimum enzymatic activity. It has been surprisingly found that a
- 30 wide range of range of substrate specificity and a high flexibility toward a variety of wash conditions can be achieved with combining further the pectate lyase of the present invention with a pectin lyase. This results in synergistic cleaning and especially plant-based soil / stains and body soil removal.
- 35 Pectin lyase enzyme is classified under the EC classification EC 4.2.2.10, is preferably substantially free of other pectic enzymes, and acts on the pectic acids

to bring about non-hydrolytic cleavage of alpha-1-4 glycosidic linkages to give oligosaccharides with terminal 4-deoxy-6- $\alpha$ -D-galacto-enuronosyl groups. The pectin lyase of the present invention is substantially free of other pectic enzymes. By "substantially free of other pectic enzymes", it is meant pectin lyase enzyme-containing compositions which contain less than 25% of pectic enzymes which are not pectin lyase enzymes, preferably less than 15%, more preferably less than 5%. The enzymatic activity can be measured according to the "Assay of trans-eliminase activities toward pectin and pectic acid" described by K. Horikoshi in Agr. Biol. Chem, Vol 36(2), 286.

Preferred pectin lyase for the purpose of the present invention is the pectin lyase described in the co-pending international patent application PCT/DK98/00514, internationally filed on November 24, 1998 and published under WO99/27083 and which is

- i) a polypeptide produced by *Bacillus licheniformis*, ATCC 14580, or
- ii) a polypeptide comprising an amino acid sequence as shown in positions 31-494 of SEQ ID NO:2 of PCT/DK98/00514, or
- iii) an analogue of the polypeptide defined in i) or ii) which is at least 60% homologous with said polypeptide, or
- iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginins in positions 377 and 383 relative to SEQ ID NO:2 of PCT/DK98/00514 are conserved and that the derived polypeptide is at least 60% homologous with said polypeptide, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE®, DURAZYM® and SAVINASE® from Novo and MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent

Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein.

5 Suitable is the protease called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16,  
10 1991. Genetically modified variants, particularly of Protease C, are also included herein.

A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality  
15 of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274  
20 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994. Also suitable is a carbonyl hydrolase variant of the protease described in WO95/10591, having an amino acid sequence derived by  
25 replacement of a plurality of amino acid residues replaced in the precursor enzyme corresponding to position +210 in combination with one or more of the following residues : +33, +62, +67, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218, and +222, where the numbered position corresponds to naturally-  
30 occurring subtilisin from *Bacillus amyloliquefaciens* or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins, such as *Bacillus lentus* subtilisin (co-pending patent application US Serial No. 60/048,550, filed June 04, 1997).

Also suitable for the present invention are proteases described in patent  
35 applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221.

See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

The proteolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

The cellulases usable in the present invention include both bacterial or fungal cellulases. Preferably, they will have a pH optimum of between 5 and 12 and a specific activity above 50 CEVU/mg (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, J61078384 and WO96/02653 which discloses fungal cellulase produced respectively from *Humicola insolens*, *Trichoderma*, *Thielavia* and *Sporotrichum*. EP 739 982 describes cellulases isolated from novel *Bacillus* species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO95/26398.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800.

Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from *Humicola insolens*, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from *Trichoderma longibrachiatum* described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and

WO91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 and WO95/24471.

Said cellulases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

5

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc and with a phenolic substrate as bleach enhancing molecule. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP 15 No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Enhancers are generally comprised at a level of from 0.1% to 5% by weight of total composition. Preferred enhancers are substituted phenothiazine and phenoxazine 10-Phenothiazinepropionic acid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substituted syringates (C3-C5 substituted alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P 35 "Amano," hereinafter referred to as "Amano-P". Other suitable commercial

lipases include Amano-CES. lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase<sup>R</sup> and Lipomax<sup>R</sup> (Gist-Brocades) and Lipolase<sup>R</sup> and Lipolase Ultra<sup>R</sup>(Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitable are the lipolytic enzymes described in EP 258 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor); WO 90/09446 (Plant Genetic System) and WO 94/14963 and WO 94/14964 (Unilever).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Amylases ( $\alpha$  and/or  $\beta$ ) can be included for removal of carbohydrate-based stains. WO94/02597, Novo Nordisk A/S published February 03, 1994, describes detergent compositions which incorporate mutant amylases. See also WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in detergent compositions include both  $\alpha$ - and  $\beta$ -amylases.  $\alpha$ -Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314, published August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases described in EP 277 216, WO95/26397 and WO96/23873 (all by Novo Nordisk).

Examples of commercial  $\alpha$ -amylases products are Purafect Ox Am<sup>®</sup> from Genencor and Termamyl<sup>®</sup>, Ban<sup>®</sup>, Fungamyl<sup>®</sup> and Duramyl<sup>®</sup>, all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases :  $\alpha$ -



amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas®  $\alpha$ -amylase activity assay. Suitable are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The amylolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimise their performance efficiency in the detergent compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability. Special attention must be paid to the cellulases as most of the cellulases have separate binding domains (CBD). Properties of such enzymes can be altered by modifications in these domains.

Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc. containing one enzyme ) or as mixtures of two or more enzymes (e.g. cocranulates ).

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Co-pending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

#### ***Colour care and fabric care benefits***

Technologies which provide a type of colour care benefit can also be included. Examples of these technologies are metallo catalysts for colour maintenance. Such metallo catalysts are described in co-pending European Patent Application No. 92870181.2. Dye fixing agents, polyolefin dispersion for anti-wrinkles and improved water absorbancy, perfume and amino-functional polymer (PCT/US97/16546) for colour care treatment and perfume substantivity are further examples of colour care / fabric care technologies and are described in the co-pending Patent Application No. 96870140.9, filed November 07, 1996.

Fabric softening agents can also be incorporated into detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and dilong-chain amides as disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0 299 575 and 0 313 146.

Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

### ***Chelating Agents***

The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilo-

triacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines. alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferably, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

### ***Suds suppressor***

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable

carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components. A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor system are described in Co-pending European Patent application N 92870174.7 filed 10 November, 1992. Especially preferred silicone suds controlling agents are described in Co-pending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil<sup>R</sup>.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

### ***Others***

Other components used in detergent compositions may be employed, such as soil-suspending agents, soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and/or encapsulated or non-encapsulated perfumes.

Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB 1,464,616. Other suitable water soluble encapsulating materials comprise dextrans derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrans are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials

include N-Lok manufactured by National Starch. The N-Lok encapsulating material consists of a modified maize starch and glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

5

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

15

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2' disulphonate, disodium 4, - 4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino-stilbene-2:2' - disulphonate, disodium 4,4' - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2' - disulphonate, monosodium 4',4'' -bis-(2,4-dianilino-s-triazin-6 ylamino)stilbene-2-sulphonate, disodium 4,4' -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2' - disulphonate, di-sodium 4,4' -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2' disulphonate, di-so-dium 4,4'bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6- ylamino)stilbene-2,2'disulphonate, sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3 - triazole-2''-sulphonate and 4,4'-bis(2-sulphostyryl)biphenyl. Highly preferred brighteners are the specific brighteners disclosed in EP 753 567.

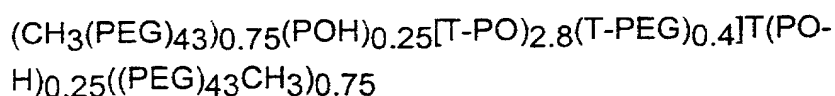
25

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning

35

performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula



where PEG is  $-(\text{OC}_2\text{H}_4)_n\text{O}-$ , PO is  $(\text{OC}_3\text{H}_6\text{O})$  and T is  $(\text{pOC}_6\text{H}_4\text{CO})$ .

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfobenzoic acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

It is well-known in the art that free chlorine in tap water rapidly deactivates the enzymes comprised in detergent compositions. Therefore, using chlorine scavenger such as perborate, ammonium sulfate, sodium sulphite or polyethyleneimine at a level above 0.1% by weight of total composition, in the formulas will provide improved through the wash stability of the detergent

enzymes. Compositions comprising chlorine scavenger are described in the European patent application 92870018.6 filed January 31, 1992.

Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula  $-(CH_2CH_2O)_m(CH_2)_nCH_3$  wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

#### 15 ***Dispersants***

The detergent composition of the present invention can also contain dispersants : Suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 1,000 to 100,000.

Especially, copolymer of acrylate and methylacrylate such as the 480N having a molecular weight of 4000, at a level from 0.5-20% by weight of composition can be added in the detergent compositions of the present invention.

The compositions of the invention may contain a lime soap peptiser compound, which has preferably a lime soap dispersing power (LSDP), as defined hereinafter of no more than 8, preferably no more than 7, most preferably no more than 6. The lime soap peptiser compound is preferably present at a level from 0% to 20% by weight.

A numerical measure of the effectiveness of a lime soap peptiser is given by the lime soap dispersant power (LSDP) which is determined using the lime soap dispersant test as described in an article by H.C. Borghetty and C.A. Bergman, J.



Am. Oil. Chem. Soc., volume 27, pages 88-90, (1950). This lime soap dispersion test method is widely used by practitioners in this art field being referred to, for example, in the following review articles; W.N. Linfield, Surfactant science Series, Volume 7, page 3; W.N. Linfield, Tenside surf. det., volume 27, pages 159-163, (1990); and M.K. Nagarajan, W.F. Masler, Cosmetics and Toiletries, volume 104, pages 71-73, (1989). The LSDP is the % weight ratio of dispersing agent to sodium oleate required to disperse the lime soap deposits formed by 0.025g of sodium oleate in 30ml of water of 333ppm  $\text{CaCO}_3$  (Ca:Mg=3:2) equivalent hardness.

Surfactants having good lime soap peptiser capability will include certain amine oxides, betaines, sulfobetaines, alkyl ethoxysulfates and ethoxylated alcohols.

Exemplary surfactants having a LSDP of no more than 8 for use in accord with the present invention include  $\text{C}_{16}$ - $\text{C}_{18}$  dimethyl amine oxide,  $\text{C}_{12}$ - $\text{C}_{18}$  alkyl ethoxysulfates with an average degree of ethoxylation of from 1-5, particularly  $\text{C}_{12}$ - $\text{C}_{15}$  alkyl ethoxysulfate surfactant with a degree of ethoxylation of amount 3 (LSDP=4), and the  $\text{C}_{14}$ - $\text{C}_{15}$  ethoxylated alcohols with an average degree of ethoxylation of either 12 (LSDP=6) or 30, sold under the tradenames Lutensol A012 and Lutensol A030 respectively, by BASF GmbH.

Polymeric lime soap peptisers suitable for use herein are described in the article by M.K. Nagarajan, W.F. Masler, to be found in Cosmetics and Toiletries, volume 104, pages 71-73, (1989).

Hydrophobic bleaches such as 4-[N-octanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-nonanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-decanoyl-6-aminohexanoyl]benzene sulfonate and mixtures thereof; and nonanoyloxy benzene sulfonate together with hydrophilic / hydrophobic bleach formulations can also be used as lime soap peptisers compounds.

### ***Dye transfer inhibition***

The detergent compositions of the present invention can also include compounds for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

### ***Polymeric dye transfer inhibiting agents***

5 The detergent compositions according to the present invention also comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.05% to 1% by weight of polymeric dye transfer inhibiting agents. Said polymeric dye transfer inhibiting agents are normally incorporated into detergent compositions in order to inhibit the transfer of dyes from colored fabrics onto fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

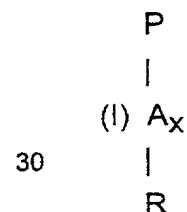
Especially suitable polymeric dye transfer inhibiting agents are polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinylloxazolidones and polyvinylimidazoles or mixtures thereof.

Addition of such polymers also enhances the performance of the enzymes according the invention.

#### 20 a) Polyamine N-oxide polymers

The polyamine N-oxide polymers suitable for use contain units having the following structure formula :

25



30

wherein P is a polymerisable unit, whereto the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.

35

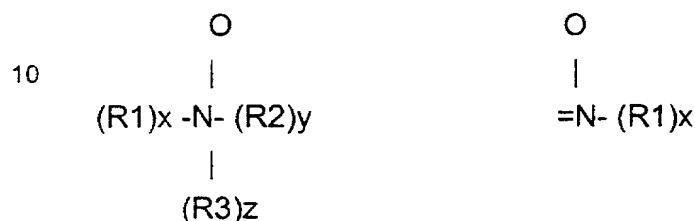




A is NC, CO, C, -O-, -S-, -N- ; x is 0 or 1;

- R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



- wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.
- The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.
- Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.
- One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.
- Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group.

5 Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups.

10 Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, 15 polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by 20 appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an 25 amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a PKa < 10, preferably PKa < 7, more preferred PKa < 6.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

30 Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

The N-vinylimidazole N-vinylpyrrolidone polymers used in the present invention have an average molecular weight range from 5,000-1,000,000, preferably from 5,000-200,000.

5 Highly preferred polymers for use in detergent compositions according to the present invention comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000.

10 The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113, "Modern Methods of Polymer Characterization".

Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have an average molecular weight range from 5,000 to 50,000; more preferably from 8,000 to 30,000; most preferably from 10,000 to 20,000.

15 The N-vinylimidazole N-vinylpyrrolidone copolymers characterized by having said average molecular weight range provide excellent dye transfer inhibiting properties while not adversely affecting the cleaning performance of detergent compositions formulated therewith.

20 The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4 .

#### c) Polyvinylpyrrolidone

25 The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000. Suitable polyvinylpyrrolidones are commercially available  
30 from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation  
35 include Sokalan HP 165 and Sokalan HP 12; polyvinylpyrrolidones known to

persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

d) Polyvinylloxazolidone :

5 The detergent compositions of the present invention may also utilize polyvinylloxazolidone as a polymeric dye transfer inhibiting agent. Said polyvinylloxazolidones have an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to  
10 about 15,000.

e) Polyvinylimidazole :

The detergent compositions of the present invention may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said  
15 polyvinylimidazoles have an average about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

f) Cross-linked polymers :

20 Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups n the backbone or on branches; cross-linked polymers have been described in the Journal of Polymer Science, volume 22, pages 1035-1039.

In one embodiment, the cross-linked polymers are made in such a way that  
25 they form a three-dimensional rigid structure, which can entrap dyes in the pores formed by the three-dimensional structure. In another embodiment, the cross-linked polymers entrap the dyes by swelling. Such cross-linked polymers are described in the co-pending patent application 94870213.9

30

**Method of washing**

The compositions of the invention may be used in essentially any washing or cleaning methods, including soaking methods, pretreatment methods and  
35 methods with rinsing steps for which a separate rinse aid composition may be added.

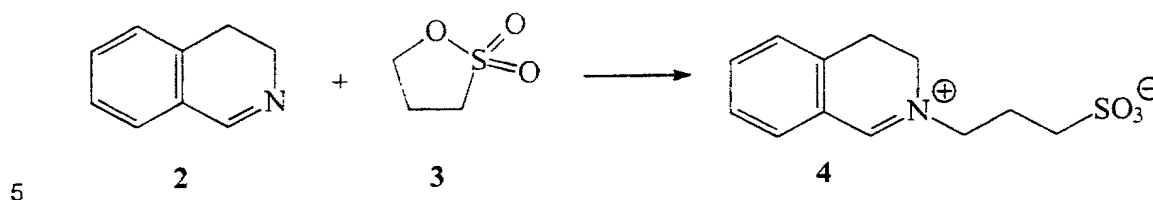
5 The process described herein comprises contacting fabrics, dishware or any other hard surface with a cleaning solution in the usual manner and exemplified hereunder. A conventional laundry method comprises treating soiled fabric with an aqueous liquid having dissolved or dispensed therein an effective amount of the laundry detergent and/or fabric care composition. A preferred machine dishwashing method comprises treating soiled articles with an aqueous liquid having dissolved or dispensed therein an effective amount of the machine dishwashing or rinsing composition. A conventional effective amount of the machine dishwashing composition means from 8-60 g of product dissolved or dispersed in a wash volume from 3-10 litres. According to a manual dishwashing method, soiled dishes are contacted with an effective amount of the dishwashing composition, typically from 0.5-20g (per 25 dishes being treated). Preferred manual dishwashing methods include the application of a concentrated solution to the surfaces of the dishes or the soaking in large volume of dilute solution of the detergent composition. A conventional hard surface method comprises treating soiled hard items/surfaces with e.g. a sponge, brush, cloth, etc. with an aqueous liquid having dissolved or dispensed therein an effective amount of the hard surface cleaner and/or with such composition undiluted. It also encompasses the soaking of a hard item in a concentrated solution or in a large volume of dilute solution of the detergent composition.

25 The process of the invention is conveniently carried out in the course of the cleaning process. The method of cleaning is preferably carried out at 5°C to 95°C, especially between 10°C and 60°C. The pH of the treatment solution is preferably from 7 to 12.

30 **Preparation example 1 : Preparation of 3-(3,4-Dihydroisoquinolinium)propane sulfonate (4)**

Into a 250 ml round-bottom flask equipped with magnetic stir bar, argon inlet, addition funnel, and reflux condenser is placed 3,4-dihydroisoquinoline (2, 5.005g) and methanol (23 ml). This mixture is cooled with an ice bath and charged dropwise with a solution of 1,3-propane sultone (3, 4.670 g) in methanol (23 ml). On complete addition the ice bath is removed and the reaction is heated to reflux overnight. The mixture is allowed to cool to room temperature and

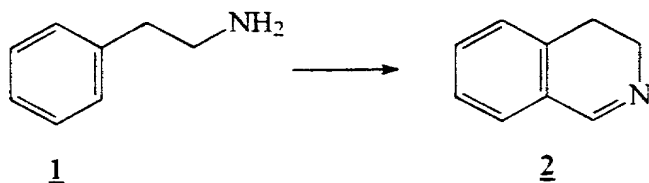
volatiles are removed under reduced pressure. The solid product is slurried and rinsed with acetone three times and allowed to air dry. The preparation is represented by the following reaction:



**Preparation example 2 :** Preparation of 1-(3,4-dihydroisoquinolinium)-decane-2-sulfate (5):

10

**Step 1:** Preparation of 3,4-dihydroisoquinoline (2):



15 A 100 mL round bottom flask equipped with stir bar and distillation apparatus is charged with phenethylamine (1, 0.0413 mol) and 88% formic acid (7.6 g, 3.5 equiv.) and the reaction is distilled or refluxed at approximately 100 °C. Beginning after one hour, additional 2 mL aliquots of 88% formic acid are added at approximately 30 minute intervals until the phenethylamine is consumed, as monitored by gas chromatography. The reaction mixture is distilled (using a

20 Dean-Stark trap) at approximately 200 °C for approximately 45 minutes after which it is allowed to cool to room temperature.

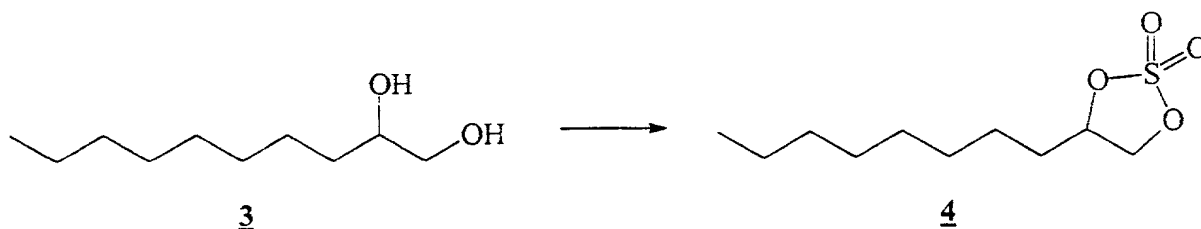
A 250 mL round bottom flask equipped with stir bar, reflux condenser, and an addition funnel is charged with phosphorus pentoxide (7.07 g) and polyphosphoric acid in a 10.5:1 weight ratio. The mixture is stirred and heated at

25 approximately 180 °C for about 1 hour, then cooled to approximately 150 °C. The cooled, crude phenethylformamide prepared as described above is added dropwise to this mixture. On complete addition the reaction is heated and stirred at approximately 170 °C overnight. The mixture is cooled to room temperature



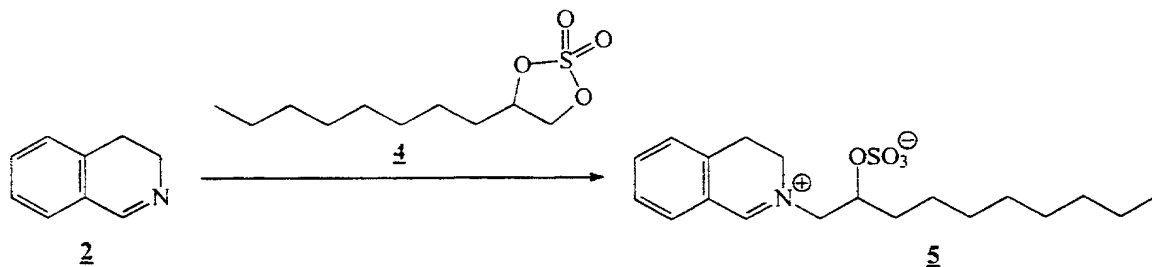
and diluted with water (300 mL), washed with diethyl ether (150 mL) and cooled in an acetone/dry ice bath while the pH is adjusted to 9 with saturated potassium hydroxide. The aqueous solution is extracted with ether (3x 150 mL) and the pooled organics are dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield an oil that is further purified via Kugelrohr distillation (70 °C, 1 mm Hg) to give the compound of formula 2.

**Step 2: Preparation of 1,2-decanediol cyclic sulfate (4):**



A three-neck, 500 mL round bottom flask equipped with mechanical stirrer, pressure equalizing addition funnel, and reflux condenser with Drierite® filled drying tube is charged with 1,2-decanediol (3, 8.72 g, 50.0 mmol) and 50 mL of carbon tetrachloride. When the 1,2-decanediol is dissolved, thionyl chloride (5.5 mL, 75 mmol) is added dropwise at room temperature and the reaction is heated to approximately 60 °C. After two hours, the reaction is slowly cooled to about 0 °C. Deionized water (50 mL) and acetonitrile (75 mL) are added. Ruthenium chloride hydrate (0.13 g, 0.50 mmol) and sodium periodate (21.4 g, 100 mmol) are added and the reaction mixture is stirred at room temperature for 1 h. The mixture is extracted with diethyl ether (4 x 175 mL), the organics are washed with deionized water (5 x 100 mL), saturated sodium bicarbonate solution (3 x 100 mL), and brine (2 x 100 mL), then filtered through celite/silica gel. The filtrate is dried over magnesium sulfate, filtered and concentrated via rotary evaporation to a clear oil.

**Step 3: Preparation of 1-(3,4-dihydroisoquinolinium)-decane-2-sulfate (5)**



A 100 mL round bottom flask equipped with magnetic stir bar is charged with 3,4-dihydroisoquinoline (2.02 g, 15.4 mmol) and acetonitrile (15.2 mL). To this is added all at once 1,2-decanediol cyclic sulfate (3.78 g, 16.0 mmole). As the reaction mixture thickens, additional acetonitrile (60 mL) is added and the reaction is stirred overnight. The precipitate is collected, washed five times with acetone, and allowed to air dry.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention. In the detergent compositions, the enzymes levels are expressed by pure enzyme by weight of the total composition and unless otherwise specified, the detergent ingredients are expressed by weight of the total compositions. The abbreviated component identifications therein have the following meanings:

LAS	: Sodium linear C <sub>11-13</sub> alkyl benzene sulphonate.
TAS	: Sodium tallow alkyl sulphate.
CxyAS	: Sodium C <sub>1x</sub> - C <sub>1y</sub> alkyl sulfate.
CxySAS	: Sodium C <sub>1x</sub> - C <sub>1y</sub> secondary (2,3) alkyl sulfate.
MBASx,y	: Sodium mid-chain branched alkyl sulfate having an average of x carbon atoms, whereof an average of y carbon atoms are comprised in (a) branching) unit(s) .
CxyEz	: C <sub>1x</sub> - C <sub>1y</sub> predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide.
CxyEzS	: C <sub>1x</sub> - C <sub>1y</sub> sodium alkyl sulfate condensed with an average of z moles of ethylene oxide.
CxEoy	: Cy alcohol with an average of ethoxylation of y.
Nonionic	: Mixed ethoxylated/propoxylated fatty alcohol e.g. Plurafac LF404 being an alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5.
QAS	: R <sub>2</sub> .N+(CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH) with R <sub>2</sub> = C <sub>12</sub> -C <sub>14</sub> .
SADS	: Sodium C <sub>14-22</sub> alkyl disulfate of the formula 2-R.C <sub>4</sub> H <sub>7</sub> .-1,4-(SO <sub>4</sub> -) <sub>2</sub> where R = C <sub>10-18</sub> .
MES	: x-sulpho methyl ester of C <sub>18</sub> fatty acid.

Soap	: Sodium linear alkyl carboxylate derived from a 80/20 mixture of tallow and coconut fatty acids.
Silicate	: Amorphous Sodium Silicate ( $\text{SiO}_2\text{:Na}_2\text{O}$ ratio = 1.6-3.2:1).
Metasilicate	: Sodium metasilicate ( $\text{SiO}_2\text{:Na}_2\text{O}$ ratio = 1.0).
Zeolite A	: Hydrated Sodium Aluminosilicate of formula $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$ having a primary particle size in the range from 0.1 to 10 micrometers (Weight expressed on an anhydrous basis).
(Na-)SKS-6	: Crystalline layered silicate of formula $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ .
Citrate	: Tri-sodium citrate dihydrate.
Citric	: Anhydrous citric acid.
Carbonate	: Anhydrous sodium carbonate.
Bicarbonate	: Sodium hydrogen carbonate.
Sulphate	: Anhydrous sodium sulphate.
STPP	: Sodium tripolyphosphate.
TSPP	: Tetrasodium pyrophosphate.
MA/AA	: Random copolymer of 4:1 acrylate/maleate, average molecular weight about 70,000-80,000.
MA/AA 1	: Random copolymer of 6:4 acrylate/maleate, average molecular weight about 10,000.
AA	: Sodium polyacrylate polymer of average molecular weight 4,500.
Polycarboxylate	: Copolymer comprising mixture of carboxylated monomers such as acrylate, maleate and methacrylate with a MW ranging between 2,000-80,000 such as Sokolan commercially available from BASF, being a copolymer of acrylic acid, MW4,500.
BB1	: 3-(3,4-Dihydroisoquinolinium)propane sulfonate as prepared in the preparation example 1
BB2	: 1-(3,4-dihydroisoquinolinium)-decane-2-sulfate as prepared in the preparation example 2
PB1	: Anhydrous sodium perborate monohydrate.
PB4	: Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ .

Percarbonate	: Anhydrous sodium percarbonate of nominal formula $2.74 \text{ Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ .
DAP 1	: Diacyl Peroxide Particle with 30% dibenzoyl peroxide, 40% sodium sulfate, 5% Acusol 480N polymer, 2% maltodextrin, 12% ethoxylated stearyl alcohol, and balance as water.
DAP 2	: Dilauroyl peroxide available from Akzo
NaDCC	: Sodium dichloroisocyanurate.
TAED	: Tetraacetyl ethylene diamine.
NOBS	: Nonanoyloxybenzene sulfonate in the form of the sodium salt.
NACA-OBS	: (6-nonamidocaproyl) oxybenzene sulfonate.
DOBS	: Decanoyl oxybenzene sulfonate in the form of the sodium salt.
DTPA	: Diethylene triamine pentaacetic acid.
HEDP	: 1,1-hydroxyethane diphosphonic acid.
DETPMP	: Diethyltriamine penta (methylene) phosphonate, marketed by Monsanto under the Trade name Dequest 2060.
EDDS	: Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt
Chelant	: Chelant selected from EEDS, HEDP, DTPA, DETPMP and/or mixtures thereof.
Catalyst	: Mn(bicyclam)Cl <sub>2</sub>
MnTACN	: Manganese 1,4,7-trimethyl-1,4,7-triazacyclononane.
Photoactivated Bleach	: Sulfonated zinc phthalocyanine encapsulated in dextrin soluble polymer.
Photoactivated Bleach 1	: Sulfonated alumino phthalocyanine encapsulated in dextrin soluble polymer.
PAAC	: Pentaamine acetate cobalt(III) salt.
Paraffin	: Paraffin oil sold under the tradename Winog 70 by Wintershall.
NaBz	: Sodium benzoate.
Pectate lyase	: Pectate lyase from <i>Bacillus agaradhaerens</i> , NCIMB 40482 or DSM 8721

- Protease : Proteolytic enzyme sold under the tradename Savinase , Alcalase, Durazym by Novo Nordisk A/S, Maxacal, Maxapem sold by Gist-Brocades and proteases described in patents WO91/06637 and/or WO95/10591 and/or EP 251 446.
- Amylase : Amylolytic enzyme sold under the tradename Purafact Ox Am<sup>R</sup> described in WO 94/18314, WO96/05295 sold by Genencor; Termamyl<sup>®</sup>, Fungamyl<sup>®</sup> and Duramyl<sup>®</sup>, all available from Novo Nordisk A/S and those described in WO95/26397 (sold under the tradename Natalase By Novo Nordisk).
- Lipase : Lipolytic enzyme sold under the tradename Lipolase Lipolase Ultra by Novo Nordisk A/S and Lipomax by Gist-Brocades.
- Cellulase : Cellulytic enzyme sold under the tradename Carezyme, Celluzyme and/or Endolase by Novo Nordisk A/S.
- Pectin lyase : Pectin lyase produced by *Bacillus licheniformis*, ATCC 14580.
- CMC : Sodium carboxymethyl cellulose.
- PVNO : Polyvinylpyridine-N-Oxide, with an average molecular weight of 50,000.
- PVPVI : Copolymer of vinylimidazole and vinylpyrrolidone, with an average molecular weight of 20,000.
- Brightener 1 : Disodium 4,4'-bis(2-sulphostyryl)biphenyl.
- Brightener 2 : Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl) stilbene-2:2'-disulfonate.
- Silicone antifoam : Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.
- Suds Suppressor : 12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form.
- Thickener : High molecular weight crosslinked polyacrylates such as Carbopol offered by B.F. Goodrich Chemical Company and Polygel.
- SRP 1 : Anionically end capped poly esters.

- QEA : bis((C<sub>2</sub>H<sub>5</sub>O)(C<sub>2</sub>H<sub>4</sub>O)<sub>n</sub>)(CH<sub>3</sub>) -N<sup>+</sup>-C<sub>6</sub>H<sub>12</sub>-N<sup>+</sup>-(CH<sub>3</sub>)  
bis((C<sub>2</sub>H<sub>5</sub>O)-(C<sub>2</sub>H<sub>4</sub>O))<sub>n</sub>, wherein n = from 20 to 30.
- PEGX : Polyethylene glycol, of a molecular weight of x.
- PEO : Polyethylene oxide, with an average molecular weight of 5,000.
- TEPAE : Tetraethylenepentaamine ethoxylate.
- BTA : Benzotriazole.
- pH : Measured as a 1% solution in distilled water at 20°C.

### 5 Example 1

The following high density and bleach-containing laundry detergent compositions were prepared according to the present invention:

	I	II	III	IV	V	VI
<b>Blown Powder</b>						
Zeolite A	12.0	-	15.0	12.0	-	15.0
Sulfate	-	5.0	-	-	5.0	-
LAS	3.0	-	3.0	3.0	-	3.0
C45AS	3.0	2.0	4.0	3.0	2.0	4.0
QAS	-	-	1.5	-	-	1.5
DETPMP	0.4	0.4	0.4	0.4	0.4	0.4
CMC	0.4	0.4	0.4	0.4	0.4	0.4
MA/AA	1.0	2.0	2.0	1.0	2.0	2.0
<b>Agglomerates</b>						
QAS	1.0	-	-	1.0	-	-
LAS	-	11.0	7.0	-	11.0	7.0
TAS	2.0	2.0	1.0	2.0	2.0	1.0
Silicate	3.0	-	4.0	3.0	-	4.0
Zeolite A	8.0	8.0	8.0	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0	8.0	8.0	4.0
<b>Agglomerate</b>						
NaSKS-6	15.0	12.0	5.0	15.0	12.0	5.0
LAS	8.0	7.0	4.0	8.0	7.0	4.0

	I	II	III	IV	V	VI
Spray On						
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
C25E3	2.0	-	2.0	2.0	-	2.0
Dry additives						
QEA	1.0	0.5	0.5	1.0	0.5	0.5
Citric/Citrate	5.0	-	2.0	5.0	-	2.0
Bicarbonate	-	3.0	-	-	3.0	-
Carbonate	8.0	15.0	10.0	8.0	15.0	10.0
TAED and/ or	6.0	-	5.0	6.0	-	5.0
NACA-OBS						
NOBS	-	2.0	-	-	2.0	-
DAP 1	-	-	-	6.7	4.8	5.2
Catalyst	0.002	-	0.02	-	0.02	-
Percarbonate or	14.0	7.0	10.0	4.15	7.0	10.0
PB1						
BB1	0.40	-	0.20	-	-	-
BB2	-	0.14	-	-	-	-
Polyethylene	-	-	0.2	-	-	0.2
oxide of MW						
5,000,000						
Bentonite clay	-	-	10.0	-	-	10.0
Citric acid	4.0	-	1.5	4.0	-	1.5
Pectate lyase	0.001	0.02	0.01	0.001	0.02	0.01
Protease	0.033	0.033	0.033	0.033	0.033	0.033
Lipase	0.008	0.008	0.008	0.008	0.008	0.008
Amylase	0.001	0.001	0.001	0.001	0.001	0.001
Cellulase	0.0014	0.0014	0.0014	0.0014	0.0014	0.0014
Silicone	5.0	5.0	5.0	5.0	5.0	5.0
antifoam						
Sulfate	-	3.0	-	-	3.0	-
Density (g/litre)	850	850	850	850	850	850
Moisture and miscellaneous				Up to 100%		

Example 2

The following high density and bleach-containing laundry detergent compositions were prepared according to the present invention:

		I	II	III
Blown Powder				
	Zeolite A	12.0	-	15.0
	Sulfate	-	5.0	-
	LAS	3.0	-	3.0
	C45AS	3.0	2.0	4.0
	QAS	-	-	1.5
	DETPMP	0.4	0.4	0.4
	CMC	0.4	0.4	0.4
	MA/AA	1.0	2.0	2.0
Agglomerates				
	QAS	1.0	-	-
	LAS	-	11.0	7.0
	TAS	2.0	2.0	1.0
	Silicate	3.0	-	4.0
	Zeolite A	8.0	8.0	8.0
	Carbonate	8.0	8.0	4.0
Agglomerate				
	NaSKS-6	15.0	12.0	5.0
	LAS	8.0	7.0	4.0
Spray On				
	Perfume	0.3	0.3	0.3
	C25E3	2.0	-	2.0
Dry additives				
	QEA	1.0	0.5	0.5
	Citric/Citrate	5.0	-	2.0
	Bicarbonate	-	3.0	-
	Carbonate	8.0	15.0	10.0
	Catalyst	0.002	0.02	0.02
	TAED and/ or NACA-OBS	6.0	-	5.0
	NOBS	-	2.0	-
	Percarbonate/ PB1	14.0	7.0	10.0



	I	II	III
Polyethylene oxide of MW 5,000,000	-	-	0.2
Bentonite clay	-	-	10.0
Citric acid	4.0	-	1.5
Pectate lyase	0.001	0.02	0.01
Protease	0.033	0.033	0.033
Lipase	0.008	0.008	0.008
Amylase	0.001	0.001	0.001
Cellulase	0.0014	0.0014	0.0014
Silicone antifoam	5.0	5.0	5.0
Sulfate	-	3.0	-
Density (g/litre)	850	850	850
Moisture and miscellaneous	Up to 100%		

Example 3

- 5 The following laundry compositions, which may be in the form of granules or tablet, were prepared according to the present invention.

	I	II	III	IV	V
Base Product					
C45 AS/TAS	8.0	5.0	3.0	3.0	3.0
LAS	8.0	-	8.0	-	7.0
C25AE3S	0.5	2.0	1.0	-	-
C25AE5/AE3	2.0	-	5.0	2.0	2.0
QAS	-	-	-	1.0	1.0
Zeolite A	20.0	18.0	11.0	-	10.0
SKS-6 (I) (dry add)	-	-	9.0	-	-
MA/AA	2.0	2.0	2.0	-	-
AA	-	-	-	-	4.0
Citrate	-	2.0	-	-	-
Citric	2.0	-	1.5	2.0	-
DTPA	0.2	0.2	-	-	-
EDDS	-	-	0.5	0.1	-
HEDP	-	-	0.2	0.1	-

	I	II	III	IV	V
PB1	3.0	5.0	10.0	-	4.0
Percarbonate	-	-	-	18.0	-
NOBS	3.0	4.0	-	-	4.0
NACA OBS	-	-	2.0	-	-
TAED	-	-	2.0	5.0	-
DAP 1	4.8	3.6	6.9	-	5.2
DAP 2	-	-	-	4.9	-
Catalyst	-	0.02	-	-	-
Carbonate	15.0	18.0	8.0	15.0	15.0
Sulphate	5.0	12.0	2.0	17.0	3.0
Silicate	-	1.0	-	-	8.0
Protease	0.033	0.033	0.033	0.046	0.033
Lipase	0.008	0.008	0.008	0.008	0.006
Amylase	0.001	0.001	0.001	0.0014	0.001
Cellulase	0.0014	0.0014	0.0014	0.01	-
Pectin lyase	0.001	-	-	-	-
Pectate lyase	0.001	0.002	0.02	0.05	0.005
Minors	0.5	0.5	0.5	0.5	0.5
Perfume	0.2	0.3	0.5	0.2	0.1

Moisture and miscellaneous

Up to 100%

Minors include Brightener / SRP1 / CMC / Photobleach / MgSO<sub>4</sub> / PVPVI/ Suds suppressor /PEG.

5

Example 4

The following laundry compositions, which may be in the form of granules or tablet, were prepared according to the present invention.

	I	II	III	IV	V
Base Product					
C45 AS/TAS	8.0	5.0	3.0	3.0	3.0
LAS	8.0	-	8.0	-	7.0
C25AE3S	0.5	2.0	1.0	-	-
C25AE5/AE3	2.0	-	5.0	2.0	2.0
QAS	-	-	-	1.0	1.0

	I	II	III	IV	V
Zeolite A	20.0	18.0	11.0	-	10.0
SKS-6 (I) (dry add)	-	-	9.0	-	-
MA/AA	2.0	2.0	2.0	-	-
AA	-	-	-	-	4.0
Citrate	-	2.0	-	-	-
Citric	2.0	-	1.5	2.0	-
DTPA	0.2	0.2	-	-	-
EDDS	-	-	0.5	0.1	-
HEDP	-	-	0.2	0.1	-
PB1	3.0	5.0	10.0	-	4.0
Percarbonate	-	-	-	18.0	-
NOBS	3.0	4.0	-	-	4.0
NACA OBS	-	-	2.0	-	-
TAED	-	-	2.0	5.0	-
BB1	0.06	-	0.34	-	0.14
BB2	-	0.14	-	0.20	-
Catalyst	-	0.001	-	-	0.002
Carbonate	15.0	18.0	8.0	15.0	15.0
Sulphate	5.0	12.0	2.0	17.0	3.0
Silicate	-	1.0	-	-	8.0
Protease	0.033	0.033	0.033	0.046	0.033
Lipase	0.008	0.008	0.008	0.008	0.006
Amylase	0.001	0.001	0.001	0.0014	0.001
Cellulase	0.0014	0.0014	0.0014	0.01	-
Pectin lyase	0.001	-	-	-	-
Pectate lyase	0.001	0.002	0.02	0.05	0.005
Minors	0.5	0.5	0.5	0.5	0.5
Perfume	0.2	0.3	0.5	0.2	0.1

Moisture and miscellaneous

Up to 100%

Minors include Brightener / SRP1 / CMC / Photobleach / MgSO<sub>4</sub> / PVPVI/ Suds suppressor /PEG.

The following high density laundry detergent compositions were prepared according to the present invention:

	I	II	III	IV	V	VI
Agglomerate						
QAS	2.0	-	2.0	2.0	-	2.0
MES	-	2.0	-	-	2.0	-
LAS	6.0	-	-	6.0	-	-
TAS	-	2.0	-	-	2.0	-
C45AS	6.0	4.0	2.0	6.0	4.0	2.0
MBAS16.5, 1.9	4.0	-	-	4.0	-	-
Zeolite A	15.0	6.0	-	15.0	6.0	-
Carbonate	4.0	8.0	4.0	4.0	8.0	4.0
MA/AA	4.0	2.0	-	4.0	2.0	-
CMC	0.5	0.5	-	0.5	0.5	-
DETPMP	0.4	0.4	-	0.4	0.4	-
Spray On						
C25E3	1.0	1.0	-	1.0	1.0	-
Perfume	0.5	0.5	0.5	0.5	0.5	0.5
Agglomerate						
SKS-6	7.0	15.0	20.0	7.0	15.0	20.0
LAS	5.8	9.0	15.0	5.8	9.0	15.0
Zeolite	-	0.9	-	-	0.9	-
Water	0.08	0.1	-	0.08	0.1	-
Dry Adds						
EDDS/HEDP	0.5	0.3	0.5	0.5	0.3	0.5
NaSKS 6 (I)	5.0	6.0	4.0	5.0	6.0	4.0
Citrate	-	1.0	-	-	1.0	-
Citric	2.0	-	2.0	2.0	-	2.0
NACA-OBS	4.1	-	5.0	4.1	-	5.0
TAED	0.8	2.0	-	0.8	2.0	-
Percarbonate	20.0	20.0	15.0	20.0	20.0	15.0
DAP 1	-	-	-	3.2	2.6	3.2
Catalyst	-	0.002	-	-	0.002	-
BB1	0.45	-	0.30	-	-	-
BB2	-	0.25	-	-	-	-

	I	II	III	IV	V	VI
SRP 1	0.3	0.3	-	0.3	0.3	-
Pectate lyase	0.002	0.01	0.03	0.002	0.01	0.03
Pectin lyase	0.001	-	-	0.001	-	-
Protease	0.046	0.046	0.033	0.046	0.046	0.033
Lipase	0.008	0.008	0.006	0.008	0.008	0.006
Cellulase	0.0014	0.0014	0.001	0.0014	0.0014	0.001
Amylase	0.001	0.001	-	0.001	0.001	-
QEA	1.0	-	1.0	1.0	-	1.0
Silicone antifoam	1.0	0.5	0.5	1.0	0.5	0.5
Brightener 1	0.2	0.2	-	0.2	0.2	-
Brightener 2	0.2	-	0.2	0.2	-	0.2
Density (g/litre)	850	850	800	850	850	800
Moisture and miscellaneous	Up to 100%					

#### Example 6

The following granular detergent were prepared in accordance with the present invention:

5

	I	II	III	IV	V	VI	VII	VIII
Base granule								
STPP	-	22.0	-	15.0	-	22.0	-	15.0
Zeolite A	30.0	-	24.0	5.0	30.0	-	24.0	5.0
Sulfate	5.5	5.0	7.0	7.0	5.5	5.0	7.0	7.0
MA/AA	3.0	-	-	-	3.0	-	-	-
AA	-	1.6	2.0	-	-	1.6	2.0	-
MA/AA (1)	-	12.0	-	6.0	-	12.0	-	6.0
LAS	14.0	10.0	9.0	20.0	14.0	10.0	9.0	20.0
C45AS	8.0	7.0	9.0	7.0	8.0	7.0	9.0	7.0
C45AE11S	-	1.0	-	1.0	-	1.0	-	1.0
MES	0.5	4.0	6.0	-	0.5	4.0	6.0	-
SADS	2.5	-	-	1.0	2.5	-	-	1.0
Silicate	-	1.0	0.5	10.0	-	1.0	0.5	10.0
Soap	-	2.0	-	-	-	2.0	-	-
Brightener 1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Carbonate	6.0	9.0	8.0	10.0	6.0	9.0	8.0	10.0

	I	II	III	IV	V	VI	VII	VIII
PEG 4000	-	1.0	1.5	-	-	1.0	1.5	-
DTPA	-	0.4	-	-	-	0.4	-	-
Spray on								
C25E9	-	-	-	5.0	-	-	-	5.0
C45E7	1.0	1.0	-	-	1.0	1.0	-	-
C23E9	-	1.0	2.5	-	-	1.0	2.5	-
Perfume	0.2	0.3	0.3	-	0.2	0.3	0.3	-
Dry additives								
Carbonate	5.0	10.0	13.0	8.0	5.0	10.0	13.0	8.0
PVPVI/PVNO	0.5	-	0.3	-	0.5	-	0.3	-
Protease	0.033	0.033	0.033	.0016	0.033	0.033	0.033	.0016
Lipase	0.008	-	-	0.008	0.008	-	-	0.008
Amylase	.0016	-	-	.0016	.0016	-	-	.0016
Cellulase	.0002	.0005	.0005	.0002	.0002	.0005	.0005	.0002
Pectate lyase	0.001	0.02	0.03	0.015	0.001	0.02	0.03	0.015
DTPA	0.5	0.3	0.5	1.0	0.5	0.3	0.5	1.0
PB1	5	3.0	10	4.0	5	3.0	10	4.0
DAP 1	-	-	-	-	3.8	6.7	4.3	3.2
Catalyst	0.001	-	-	0.002	-	0.001	-	-
BB1	0.2	-	-	0.5	-	-	-	-
BB2	-	0.3	0.4	-	-	-	-	-
NOBS/ TAED	0.5	0.3	0.5	0.6	0.5	0.3	0.5	0.6
Sulfate	4.0	5.0	-	5.0	4.0	5.0	-	5.0
SRP1	-	0.4	-	-	-	0.4	-	-
Sud supressor	-	0.5	-	-	-	0.5	-	-
speckle	0.9	-	2.7	1.2	0.9	-	2.7	1.2
Moisture and miscellaneous	Up to 100%							

Example 7

- 5 The following laundry detergent compositions were prepared in accordance with the present invention:

	I	II	III	IV	V	VI	VII
LAS	12.0	16.0	23.0	19	18.0	20.0	16.0

	I	II	III	IV	V	VI	VII
C45AS		4.5	-		-	-	4.0
C45 E3S	-	-	2.0	-	1.0	1.0	1.0
C45E6.5S	2.0	2.0	-	1.3	-	-	0.6
C <sub>9</sub> -C <sub>14</sub> alkyl dimethyl hydroxy ethyl quaternary NH <sub>4</sub> salt			-	-	1.0	0.5	2.0
Tallow fatty acid	-	-	-	-	-	-	1.0
STPP	23.0	25.0	24.0	22.0	20.0	15.0	20.0
Carbonate	15.0	12.0	15.0	10.0	13.0	11.0	10.0
Sodium Polyacrylate (45%)	0.5	0.5	0.5	0.5	-	-	-
MA/AA	-	-	1.0	1.0	1.0	2.0	0.5
Silicate (1:6 ratio	3.0	6.0	9.0	8.0	9.0	6.0	8.0
Sulfate	25.0	18.0	20.0	18.0	20.0	22.0	13.0
PB1	5.0	5.0	10.0	8.0	3.0	1.0	2.0
PEG MW4000 (50%)	1.5	1.5	1.0	1.0	-	-	0.5
CMC	1.0	1.0	1.0	-	0.5	0.5	0.5
NOBS/ DOBS	0.5	1.0	0.5	0.5	1.0	0.7	0.3
TAED	1.5	1.0	2.5	3.0	0.3	0.2	0.5
BB1	-	0.3	-	0.5	0.3	-	0.25
BB2	0.4	-	0.4	-	0.3	0.4	-
SRP1	1.5	1.5	1.0	1.0	-	1.0	-
SRP2	-	-	-	-	1.0	-	1.0
Moisture	7.5	7.5	6.0	7.0	5.0	3.0	5.0
Mg sulphate	-	-	-	-	1.0	0.5	1.5
Chelant	-	-	-	-	0.8	0.6	1.0
Protease	0.033	0.033	0.033	0.046	0.033	0.033	0.033
Lipase	0.008	0.008	0.008	0.008	0.006	-	-
Amylase	0.001	0.001	0.001	.0014	0.001	-	-
Cellulase	.0014	.0014	.0014	0.01	-	.0005	.0005
Pectate lyase	0.001	0.02	0.01	0.001	0.002	0.015	0.03
Pectin lyase	0.001	-	-	0.001	0.001	-	-
speckle	2.5	4.1	4.2	4.4	5.6	5.0	5.2
Minors	1.0	1.0	1.0	1.0	0.5	1.5	1.0

Example 8

The following laundry detergent compositions were prepared in accordance with the present invention:

5

	I	II	III	IV	V	VI	VII
LAS	12.0	16.0	23.0	19	18.0	20.0	16.0
C45AS		4.5	-		-	-	4.0
C45 E0.5S			-	-	-	-	-
C45 E3S	-	-	2.0	-	1.0	1.0	1.0
C45E6.5S	2.0	2.0	-	1.3	-	-	0.6
C <sub>9</sub> -C <sub>14</sub> alkyl dimethyl hydroxy ethyl quaternary NH <sub>4</sub> salt			-	-	1.0	0.5	2.0
Tallow fatty acid			-	-	-	-	1.0
Tallow alcohol ethoxylate (50)	-	-	-	-	-	-	-
STPP	23.0	25.0	24.0	22.0	20.0	15.0	20.0
Carbonate	15.0	12.0	15.0	10.0	13.0	11.0	10.0
Sodium Polyacrylate (45%)	0.5	0.5	0.5	0.5	-	-	-
MA/AA	-	-	1.0	1.0	1.0	2.0	0.5
Silicate (1:6 ratio)	3.0	6.0	9.0	8.0	9.0	6.0	8.0
Sulfate	25.0	18.0	20.0	18.0	20.0	22.0	13.0
PB1	5.0	5.0	10.0	8.0	3.0	1.0	2.0
PEG MW ~4000 (50%)	1.5	1.5	1.0	1.0	-	-	0.5
CMC	1.0	1.0	1.0	-	0.5	0.5	0.5
Citric	-	-	-	-	-	-	-
Catalyst	0.05	0.005	0.1	0.002	0.02	0.05	0.005
NOBS/ DOBS	0.5	1.0	0.5	0.5	1.0	0.7	0.3
TAED	1.5	1.0	2.5	3.0	0.3	0.2	0.5
SRP1	1.5	1.5	1.0	1.0	-	1.0	-
SRP2	-	-	-	-	1.0	-	1.0
Moisture	7.5	7.5	6.0	7.0	5.0	3.0	5.0
Mg sulphate	-	-	-	-	1.0	0.5	1.5
Chelant	-	-	-	-	0.8	0.6	1.0



	I	II	III	IV	V	VI	VII
Protease	0.033	0.033	0.033	.0016	0.033	0.016	0.033
Lipase	0.008	-	-	0.008	0.006	-	0.008
Amylase	.0016	-	-	.0016	0.001	0.001	.0016
Cellulase	.0002	.0005	.0005	.0002	-	.0015	.0002
Pectate lyase	0.001	0.02	0.01	0.001	0.002	0.015	0.03
Pectin lyase	0.001	-	-	0.001	0.001	-	-
speckle	2.5	4.1	4.2	4.4	5.6	5.0	5.2
Minors	1.0	1.0	1.0	1.0	0.5	1.5	1.0

### Example 9

The following laundry detergent compositions were prepared in accordance with the present invention:

	I	II	III	IV	V	VI	VII	VIII
LAS	13.3	13.7	10.4	8.0	13.3	13.7	10.4	8.0
C <sub>45</sub> AS	3.9	4.0	4.5	-	3.9	4.0	4.5	-
C <sub>45</sub> E0.5S	2.0	2.0	-	-	2.0	2.0	-	-
C <sub>45</sub> E3S	-	-	-	-	-	-	-	-
C <sub>45</sub> E6.5S	0.5	0.5	0.5	5.0	0.5	0.5	0.5	5.0
C <sub>9</sub> -C <sub>14</sub> alkyl dimethyl hydroxy ethyl quaternary NH <sub>4</sub> salt	1.0	-	-	0.5	1.0	-	-	0.5
Tallow fatty acid	0.5	-	-	-	0.5	-	-	-
Tallow alcohol ethoxylate (50)	-	-	1.0	0.3	-	-	1.0	0.3
STPP	-	41.0	-	20.0	-	41.0	-	20.0
Zeolite A	26.3	-	21.3	1.0	26.3	-	21.3	1.0
Carbonate	23.9	12.4	25.2	17.0	23.9	12.4	25.2	17.0
Sodium Polyacrylate (45%)	3.4	0.0	2.7	-	3.4	0.0	2.7	-
MA/AA	-	-	1.0	1.5	-	-	1.0	1.5
Silicate (1:6 ratio)	2.4	6.4	2.1	6.0	2.4	6.4	2.1	6.0
Sulfate	10.5	10.9	8.2	15.0	10.5	10.9	8.2	15.0

			I	II	III	IV	V	VI	VII	VIII
PB1			1.0	1.0	1.0	2.0	1.0	1.0	1.0	2.0
PEG	MW	4000	1.7	0.4	1.0	-	1.7	0.4	1.0	-
(50%)										
CMC			1.0	-	-	0.3	1.0	-	-	0.3
Citric			-	-	3.0	-	-	-	3.0	-
BB1			1.0	0.5	0.6	-	-	-	-	-
BB2			-	0.2	-	1.0	-	-	-	-
DAP 1			-	-	-	-	2.0	2.1	3.4	2.1
NOBS/ DOBS			0.2	0.5	0.5	0.1	-	-	-	-
TAED			0.6	0.5	0.4	0.3	-	-	-	-
SRP 1			1.5	-	-	-	1.5	-	-	-
SRP2			-	1.5	1.0	1.0	-	1.5	1.0	1.0
Moisture			7.5	3.1	6.1	7.3	7.5	3.1	6.1	7.3
Mn sulphate			-	-	-	1.0	-	-	-	1.0
Chelant			-	-	-	0.5	-	-	-	0.5
speckles			0.5	1.0	3.0	0.5	0.5	1.0	3.0	0.5
Protease			0.033	0.033	0.033	0.046	0.033	0.033	0.033	0.046
Lipase			0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008
Amylase			0.001	0.001	0.001	.0014	0.001	0.001	0.001	.0014
Cellulase			.0014	.0014	.0014	0.01	.0014	.0014	.0014	0.01
Pectate lyase			0.001	0.01	0.005	0.002	0.001	0.01	0.005	0.002
Minors			1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Example 10

The following laundry compositions, which may be in the form of granules or  
 5 tablet, were prepared according to the present invention.

	I	II	III	IV	V
Base Product					
C45 AS/TAS	8.0	5.0	3.0	3.0	3.0
LAS	8.0	-	8.0	-	7.0
C25AE3S	0.5	2.0	1.0	-	-
C25AE5/AE3	2.0	-	5.0	2.0	2.0
QAS	-	-	-	1.0	1.0

	I	II	III	IV	V
Zeolite A	20.0	18.0	11.0	-	10.0
SKS-6 (I) (dry add)	-	-	9.0	-	-
MA/AA	2.0	2.0	2.0	-	-
AA	-	-	-	-	4.0
Citrate	-	2.0	-	-	-
Citric	2.0	-	1.5	2.0	-
DTPA	0.2	0.2	-	-	-
EDDS	-	-	0.5	0.1	-
HEDP	-	-	0.2	0.1	-
Catalyst	0.05	0.005	0.01	0.002	0.02
PB1	3.0	5.0	10.0	-	4.0
Percarbonate	-	-	-	18.0	-
NOBS	3.0	4.0	-	-	4.0
NACA OBS	-	-	2.0	-	-
TAED	-	-	2.0	5.0	-
Carbonate	15.0	18.0	8.0	15.0	15.0
Sulphate	5.0	12.0	2.0	17.0	3.0
Silicate	-	1.0	-	-	8.0
Protease	0.033	0.033	0.033	0.046	0.046
Lipase	0.008	0.008	0.008	0.008	0.008
Amylase	0.001	0.001	0.001	0.0014	0.0014
Cellulase	0.0014	0.0014	0.0014	0.01	0.01
Pectate lyase	0.001	0.002	0.02	0.05	0.005
Minors	0.5	0.5	0.5	0.5	0.5
Perfume	0.2	0.3	0.5	0.2	0.1

Moisture and miscellaneous

Up to 100%

Minors include Brightener / SRP1 / CMC / Photobleach / MgSO<sub>4</sub> / PVPVI/ Suds suppressor /PEG.

5

#### Example 11

The following high density laundry detergent compositions were prepared according to the present invention:

I II III IV

	I	II	III	IV
Agglomerate				
QAS	2.0	-	2.0	-
MES	-	2.0	-	-
LAS	6.0	-	-	-
TAS	-	2.0	-	-
C45AS	6.0	4.0	2.0	-
MBAS16.5, 1.9	4.0	-	-	-
Zeolite A	15.0	6.0	-	-
Carbonate	4.0	8.0	4.0	8.0
MA/AA	4.0	2.0	-	2.0
CMC	0.5	0.5	-	0.5
DETPMP	0.4	0.4	-	0.5
Spray On				
C25E3	1.0	1.0	-	-
Perfume	0.5	0.5	0.5	0.5
Agglomerate				
SKS-6	7.0	15.0	20.0	10.0
LAS	5.8	9.0	15.0	10.0
Zeolite	-	0.9	-	-
C45 AS	-	3.0	-	-
Water	0.08	0.1	-	0.2
Dry Adds				
EDDS/HEDP	0.5	0.3	0.5	0.8
NaSKS 6)	5.0	6.0	4.0	11.0
Citrate	-	1.0	-	-
Citric	2.0	-	2.0	4.0
Catalyst	0.005	0.1	0.02	0.02
NACA-OBS	4.1	-	5.0	4.0
TAED	0.8	2.0	-	2.0
Percarbonate	20.0	20.0	15.0	17.0
SRP 1	0.3	0.3	-	0.3
Pectate lyase	0.01	0.02	0.001	0.002
Pectin lyase	-	-	0.001	0.001
Protease	0.046	0.046	0.033	0.016
Lipase	0.008	0.008	0.006	-

	I	II	III	IV
Cellulase	0.0014	0.0014	0.001	0.001
Amylase	0.003	0.003	-	0.0015
QEA	1.0	-	1.0	1.0
Silicone antifoam	1.0	0.5	0.5	1.5
Brightener 1	0.2	0.2	-	6.2
Brightener 2	0.2	-	0.2	-
Density (g/litre)	850	850	800	775
Moisture and miscellaneous	Up to 100%			

### Example 12

- 5 The following granular fabric detergent compositions which provide "softening through the wash" capability were prepared according to the present invention :

	I	II	III	IV
C45AS	-	10.0	-	10.0
LAS	7.6	-	7.6	-
C68AS	1.3	-	1.3	-
C45E7	4.0	-	4.0	-
C25E3	-	5.0	-	5.0
Coco-alkyl-dimethyl hydroxy-ethyl ammonium chloride	1.4	1.0	1.4	1.0
Citrate	5.0	3.0	5.0	3.0
Na-SKS-6	-	11.0	-	11.0
Zeolite A	15.0	15.0	15.0	15.0
MA/AA	4.0	4.0	4.0	4.0
DETPMP	0.4	0.4	0.4	0.4
DAP 1	4.8	6.7	-	-
Catalyst	-	-	0.001	0.001
Percarbonate	-	-	-	15.0
PB1	-	-	15.0	-
TAED	-	-	5.0	5.0
Smectite clay	10.0	10.0	10.0	10.0
HMWPEO	-	0.1	-	0.1
Pectate lyase	0.001	0.01	0.001	0.01

	I	II	III	IV
Protease	0.02	0.01	0.02	0.01
Lipase	0.02	0.01	0.02	0.01
Amylase	0.03	0.005	0.03	0.005
Cellulase	0.001	-	0.001	-
Silicate	3.0	5.0	3.0	5.0
Carbonate	10.0	10.0	10.0	10.0
Suds suppressor	1.0	4.0	1.0	4.0
CMC	0.2	0.1	0.2	0.1
Miscellaneous and minors	Up to 100%			

Example 13

- 5 The following liquid detergent formulations were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

	I	II	III	IV	V
LAS	11.5	9.0	-	4.0	-
C25E2.5S	-	3.0	18.0	-	16.0
C45E2.25S	11.5	3.0	-	16.0	-
C23E9	-	3.0	2.0	2.0	1.0
C23E7	3.2	-	-	-	-
CFAA	-	-	5.0	-	3.0
TPKFA	2.0	-	2.0	0.5	2.0
Citric (50%)	6.5	1.0	2.5	4.0	2.5
Ca formate	0.1	0.06	0.1	-	-
Na formate	0.5	0.06	0.1	0.05	0.05
SCS	4.0	1.0	3.0	1.2	-
Borate	0.6	-	3.0	2.0	3.0
Na hydroxide	6.0	2.0	3.5	4.0	3.0
Ethanol	2.0	1.0	4.0	4.0	3.0
1,2 Propanediol	3.0	2.0	8.0	8.0	5.0
Monoethanolamine	3.0	1.5	1.0	2.5	1.0
TEPAE	2.0	-	1.0	1.0	1.0
Catalyst	0.01	0.01	0.005	0.005	0.1

	I	II	III	IV	V
Pectate lyase	0.001	0.002	0.01	0.01	0.005
Protease	0.03	0.01	0.03	0.02	0.02
Lipase	-	-	0.002	-	-
Amylase	-	-	-	0.002	-
Cellulase	-	-	0.0002	0.0005	0.0001
SRP 1	0.2	-	0.1	-	-
DTPA	-	-	0.3	-	-
PVNO	-	-	0.3	-	0.2
Brightener 1	0.2	0.07	0.1	-	-
Silicone antifoam	0.04	0.02	0.1	0.1	0.1
Miscellaneous and water					

#### Example 14

- 5 The following laundry bar detergent compositions were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

	I	II	III	VI	V	III	VI	V
LAS	-	-	19.0	15.0	21.0	6.75	8.8	-
C28AS	30.0	13.5	-	-	-	15.75	11.2	22.5
Na Laurate	2.5	9.0	-	-	-	-	-	-
Zeolite A	2.0	1.25	-	-	-	1.25	1.25	1.25
Carbonate	20.0	3.0	13.0	8.0	10.0	15.0	15.0	10.0
Ca Carbonate	27.5	39.0	35.0	-	-	40.0	-	40.0
Sulfate	5.0	5.0	3.0	5.0	3.0	-	-	5.0
TSPP	5.0	-	-	-	-	5.0	2.5	-
STPP	5.0	15.0	10.0	-	-	7.0	8.0	10.0
Bentonite clay	-	10.0	-	-	5.0	-	-	-
DETPMP	-	0.7	0.6	-	0.6	0.7	0.7	0.7
CMC	-	1.0	1.0	1.0	1.0	-	-	1.0
Talc	-	-	10.0	15.0	10.0	-	-	-
Silicate	-	-	4.0	5.0	3.0	-	-	-
PVNO	0.02	0.03	-	0.01	-	0.02	-	-
MA/AA	0.4	1.0	-	-	0.2	0.4	0.5	0.4

	I	II	III	VI	V	III	VI	V
SRP 1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Pectate lyase	0.01	0.001	0.005	0.02	0.02	0.001	0.01	0.01
Amylase	-	-	0.01	-	-	-	0.002	-
Protease	-	0.004	-	0.003	0.003	-	-	0.003
Lipase	-	0.002	-	0.002	-	-	-	-
Cellulase	-	.0003	-	-	.0003	.0002	-	-
Catalyst	1.0	5.0	0.1	3.0	10.0	1.0	0.3	1.0
PEO	-	0.2	-	0.2	0.3	-	-	0.3
Perfume	1.0	0.5	0.3	0.2	0.4	-	-	0.4
Mg sulfate	-	-	3.0	3.0	3.0	-	-	-
Brightener	0.15	0.1	0.15	-	-	-	-	0.1
Photoactivated bleach (ppm)	-	15.0	15.0	15.0	15.0	-	-	15.0

#### Example 15

- 5 The following laundry bar detergent compositions were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

	I	II	III	IV	V	VI	VII	VIII
LAS	-	-	19.0	15.0	21.0	6.75	8.8	-
C28AS	30.0	13.5	-	-	-	15.75	11.2	22.5
Na Laurate	2.5	9.0	-	-	-	-	-	-
Zeolite A	2.0	1.25	-	-	-	1.25	1.25	1.25
Carbonate	20.0	3.0	13.0	8.0	10.0	15.0	15.0	10.0
Ca Carbonate	27.5	39.0	35.0	-	-	40.0	-	40.0
Sulfate	5.0	5.0	3.0	5.0	3.0	-	-	5.0
TSP	5.0	-	-	-	-	5.0	2.5	-
STPP	5.0	15.0	10.0	-	-	7.0	8.0	10.0
Bentonite clay	-	10.0	-	-	5.0	-	-	-
DETPMP	-	0.7	0.6	-	0.6	0.7	0.7	0.7
CMC	-	1.0	1.0	1.0	1.0	-	-	1.0
Talc	-	-	10.0	15.0	10.0	-	-	-
Silicate	-	-	4.0	5.0	3.0	-	-	-



	I	II	III	IV	V	VI	VII	VIII
PVNO	0.02	0.03	-	0.01	-	0.02	-	-
MA/AA	0.4	1.0	-	-	0.2	0.4	0.5	0.4
SRP 1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Pectate lyase	0.01	0.001	0.005	0.02	0.02	0.1	0.01	0.01
Amylase	-	-	0.01	-	-	-	0.002	-
Protease	-	0.004	-	0.003	0.003	-	-	0.003
Lipase	-	0.002	-	0.002	-	-	-	-
Cellulase	-	.0003	-	-	.0003	.0002	-	-
PEO	-	0.2	-	0.2	0.3	-	-	0.3
Perfume	1.0	0.5	0.3	0.2	0.4	-	-	0.4
Mg sulfate	-	-	3.0	3.0	3.0	-	-	-
Brightener	0.15	0.1	0.15	-	-	-	-	0.1
DAP 1	0.4	0.6	0.8	1.0	-	-	0.2	1.0
DAP 2	-	-	-	-	1.0	1.0	0.8	-
Photoactivated bleach (ppm)	-	15.0	15.0	15.0	15.0	-	-	15.0

#### Example 16

- 5 The following laundry bar detergent compositions were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

	I	II	III	IV	V	VI	VII	VIII
LAS	-	-	19.0	15.0	21.0	6.75	8.8	-
C28AS	30.0	13.5	-	-	-	15.75	11.2	22.5
Na Laurate	2.5	9.0	-	-	-	-	-	-
Zeolite A	2.0	1.25	-	-	-	1.25	1.25	1.25
Carbonate	8.0	3.0	1.0	8.0	10.0	15.0	3.0	10.0
Ca Carbonate	27.5	27.0	35.0	-	-	28.0	-	28.0
Sulfate	5.0	5.0	3.0	5.0	3.0	-	-	5.0
TSPP	5.0	-	-	-	-	5.0	2.5	-
STPP	5.0	15.0	10.0	-	-	7.0	8.0	10.0
Bentonite clay	-	10.0	-	-	5.0	-	-	-
DETPMP	-	0.7	0.6	-	0.6	0.7	0.7	0.7

	I	II	III	IV	V	VI	VII	VIII
CMC	-	1.0	1.0	1.0	1.0	-	-	1.0
Talc	-	-	10.0	15.0	10.0	-	-	-
Silicate	-	-	4.0	5.0	3.0	-	-	-
PVNO	0.02	0.03	-	0.01	-	0.02	-	-
MA/AA	0.4	1.0	-	-	0.2	0.4	0.5	0.4
SRP 1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Pectate lyase	0.01	0.001	0.005	0.02	0.02	0.1	0.01	0.01
Pectin lyase	-	0.001	-	-	-	-	-	-
Amylase	-	-	0.01	-	-	-	0.002	-
Protease	-	0.004	-	0.003	0.003	-	-	0.003
Lipase	-	0.002	-	0.002	-	-	-	-
Cellulase	-	.0003	-	-	.0003	.0002	-	-
PEO	-	0.2	-	0.2	0.3	-	-	0.3
Perfume	1.0	0.5	0.3	0.2	0.4	-	-	0.4
Mg sulfate	-	-	3.0	3.0	3.0	-	-	-
Brightener	0.15	0.1	0.15	-	-	-	-	0.1
Catalyst	0.001	-	-	0.001	-	-	-	-
BB1	0.2	0.2	0.3	-	-	0.4	-	-
BB2	-	-	-	0.4	0.5	-	0.45	0.3
TAED	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
PB4	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0
NOBS	0.2	0.2	0.2	0.20	0.2	0.2	0.2	0.2
Photoactivated bleach (ppm)	-	15.0	15.0	15.0	15.0	-	-	15.0

Example 17

The following compact high density (0.96Kg/l) dishwashing detergent compositions were prepared according to the present invention :

	I	II	III	IV	V	VI
STPP	-	51.0	51.0	-	-	44.3
Citrate	17.0	-	-	50.0	40.2	-
Carbonate	17.5	14.0	20.0	-	8.0	33.6
Bicarbonate	-	-	-	26.0	-	-
Silicate	15.0	15.0	8.0	-	25.0	3.6
Metasilicate	2.5	4.5	4.5	-	-	-
PB1	10.0	8.0	8.0	-	-	-
PB4	-	-	-	10.0	-	-
Percarbonate	-	-	-	-	11.8	4.8
BB1	-	0.1	0.1	-	0.5	-
BB2	0.2	0.05	-	0.1	-	0.6
Nonionic	2.0	1.5	1.5	3.0	1.9	5.9
TAED	2.0	-	-	4.0	-	1.4
HEDP	1.0	-	-	-	-	-
DETPMP	0.6	-	-	-	-	-
MnTACN	-	-	-	-	0.01	-
PAAC	-	0.01	0.01	-	-	-
Paraffin	0.5	0.4	0.4	0.6	-	-
Pectate lyase	0.04	0.1	0.03	0.5	0.005	0.005
Protease	0.072	0.053	0.053	0.026	0.059	0.01
Amylase	0.012	0.012	0.012	0.021	0.021	0.006
Lipase	-	0.001	-	0.005	-	-
BTA	0.3	0.2	0.2	0.3	0.3	0.3
Polycarboxylate	6.0	-	-	-	4.0	0.9
Perfume	0.2	0.1	0.1	0.2	0.2	0.2
pH	11.0	11.0	11.3	9.6	10.8	10.9
5 Miscellaneous, sulfate and water	Up to 100%					

Example 18

The following granular dishwashing detergent compositions of bulk density 1.02Kg/L were prepared according to the present invention :

	I	II	III	IV	V	VI
STPP	30.0	33.5	27.9	29.6	33.8	22.0
Carbonate	30.5	30.5	30.5	23.0	34.5	45.0
Silicate	7.0	7.5	12.6	13.3	3.2	6.2
Metasilicate	-	4.5	-	-	-	-
Percarbonate	-	-	-	-	4.0	-
PB1	4.4	4.5	4.3	-	-	-
BB1	-	0.3	-	0.2	-	-
BB2	0.4	-	0.2	-	0.6	0.4
Nonionic	1.0	0.7	1.0	1.9	0.7	0.5
TAED	1.0	-	-	-	0.9	-
PAAC	-	0.004	-	-	-	-
Paraffin	0.25	0.25	-	-	-	-
Pectate lyase	0.4	0.005	0.001	0.02	0.02	0.1
Protease	0.036	0.021	0.03	-	0.006	-
Amylase	0.03	0.005	0.004	-	0.005	-
Lipase	0.005	-	0.001	-	-	-
BTA	0.15	0.15	-	-	0.2	-
Perfume	0.2	0.2	0.05	0.1	0.2	-
pH	10.8	11.3	11.0	10.7	11.5	10.9
5 Miscellaneous, sulfate and water	Up to 100%					

Example 19

- 10 The following tablet detergent compositions were prepared according to the present invention by compression of a granular dishwashing detergent composition at a pressure of 13KN/cm<sup>2</sup> using a standard 12 head rotary press:

	I	II	III	IV	V	VI	VII	VIII
STPP	-	48.8	54.7	38.2	-	52.4	56.1	36.0
Citrate	20.0	-	-	-	35.9	-	-	-
Carbonate	20.0	5.0	14.0	15.4	8.0	23.0	20.0	28.0

	I	II	III	IV	V	VI	VII	VIII
Silicate	15.0	14.8	15.0	12.6	23.4	2.9	4.3	4.2
Pectate lyase	0.001	0.001	0.01	0.004	0.02	0.02	0.001	0.005
Protease	0.042	0.072	0.042	0.031	0.052	0.023	0.023	0.029
Amylase	0.012	0.012	0.012	0.007	0.015	0.003	0.017	0.002
Lipase	0.005	-	-	-	-	-	-	-
PB1	14.3	7.8	11.7	12.2	-	-	6.7	8.5
PB4	-	-	-	-	22.8	-	3.4	-
Percarbonate	-	-	-	-	-	10.4	-	-
BB1	0.2	-	0.5	-	0.3	0.2	-	-
BB2	-	0.2	-	0.5	-	-	0.1	0.2
Nonionic	1.5	2.0	2.0	2.2	1.0	4.2	4.0	6.5
PAAC	-	-	0.02	0.009	-	-	-	-
MnTACN	-	-	-	-	0.007	-	-	-
TAED	2.7	2.4	-	-	-	2.1	0.7	1.6
HEDP	1.0	-	-	0.9	-	0.4	0.2	-
DETPMP	0.7	-	-	-	-	-	-	-
Paraffin	0.4	0.5	0.5	0.5	-	-	0.5	-
BTA	0.2	0.3	0.3	0.3	0.3	0.3	0.3	-
Polycarboxylate	4.0	-	-	-	4.9	0.6	0.8	-
PEG	-	-	-	-	-	2.0	-	2.0
Glycerol	-	-	-	-	-	0.4	-	0.5
Perfume	-	-	-	0.05	0.2	0.2	0.2	0.2
Weight of tablet	20g	25g	20g	30g	18g	20g	25g	24g
pH	10.7	10.6	10.7	10.7	10.9	11.2	11.0	10.8
Miscellaneous, sulfate and water	Up to 100%							

### Example 20

- 5 The following compact high density (0.96Kg/l) dishwashing detergent compositions were prepared according to the present invention :

	I	II	III	IV	V	VI
STPP	-	51.0	51.0	-	-	44.3
Citrate	17.0	-	-	50.0	40.2	-
Carbonate	17.5	14.0	20.0	-	8.0	33.6

	I	II	III	IV	V	VI
Bicarbonate	-	-	-	26.0	-	-
Silicate	15.0	15.0	8.0	-	25.0	3.6
Metasilicate	2.5	4.5	4.5	-	-	-
PB1	10.0	8.0	8.0	-	-	-
PB4	-	-	-	10.0	-	-
Percarbonate	-	-	-	-	11.8	4.8
Nonionic	2.0	1.5	1.5	3.0	1.9	5.9
DAP 1	0.2	1.0	4.3	6.7	1.7	0.3
TAED	2.0	-	-	4.0	-	1.4
HEDP	1.0	-	-	-	-	-
DETPMP	0.6	-	-	-	-	-
MnTACN	-	-	-	-	0.01	-
PAAC	-	0.01	0.01	-	-	-
Paraffin	0.5	0.4	0.4	0.6	-	-
Pectate lyase	0.04	0.001	0.03	0.005	0.005	0.005
Protease	0.072	0.053	0.053	0.026	0.059	0.01
Amylase	0.012	0.012	0.012	0.021	0.021	0.006
Lipase	-	0.001	-	0.005	-	-
BTA	0.3	0.2	0.2	0.3	0.3	0.3
Polycarboxylate	6.0	-	-	-	4.0	0.9
Perfume	0.2	0.1	0.1	0.2	0.2	0.2
pH	11.0	11.0	11.3	9.6	10.8	10.9
Miscellaneous, sulfate and water	Up to 100%					

#### Example 21

- 5 The following granular dishwashing detergent compositions of bulk density 1.02Kg/L were prepared according to the present invention :

	I	II	III	IV	V	VI
STPP	30.0	33.5	27.9	29.6	33.8	22.0
Carbonate	30.5	30.5	30.5	23.0	34.5	45.0
Silicate	7.0	7.5	12.6	13.3	3.2	6.2
Metasilicate	-	4.5	-	-	-	-
Percarbonate	-	-	-	-	4.0	-

	I	II	III	IV	V	VI
DAP 1	3.3	6.7	0.03	0.5	10.0	0.03
PB1	4.4	4.5	4.3	-	-	-
NADCC	-	-	-	2.0	-	0.9
Nonionic	1.0	0.7	1.0	1.9	0.7	0.5
TAED	1.0	-	-	-	0.9	-
PAAC	-	0.004	-	-	-	-
Paraffin	0.25	0.25	-	-	-	-
Pectate lyase	0.4	0.005	0.001	0.02	0.02	0.1
Protease	0.036	0.021	0.03	-	0.006	-
Amylase	0.03	0.005	0.004	-	0.005	-
Lipase	0.005	-	0.001	-	-	-
BTA	0.15	0.15	-	-	0.2	-
Perfume	0.2	0.2	0.05	0.1	0.2	-
pH	10.8	11.3	11.0	10.7	11.5	10.9
Miscellaneous, sulfate and water	Up to 100%					

### Example 22

- 5 The following tablet detergent compositions were prepared according to the present invention by compression of a granular dishwashing detergent composition at a pressure of 13KN/cm<sup>2</sup> using a standard 12 head rotary press:

	I	II	III	IV	V	VI	VII	VIII
STPP	-	48.8	54.7	38.2	-	52.4	56.1	36.0
Citrate	20.0	-	-	-	35.9	-	-	-
Carbonate	20.0	5.0	14.0	15.4	8.0	23.0	20.0	28.0
Silicate	15.0	14.8	15.0	12.6	23.4	2.9	4.3	4.2
Pectate lyase	0.1	0.001	0.01	0.4	0.02	0.02	0.1	0.005
Protease	0.042	0.072	0.042	0.031	0.052	0.023	0.023	0.029
Amylase	0.012	0.012	0.012	0.007	0.015	0.003	0.017	0.002
Lipase	0.005	-	-	-	-	-	-	-
PB1	14.3	7.8	11.7	12.2	-	-	6.7	8.5
PB4	-	-	-	-	22.8	-	3.4	-
Percarbonate	-	-	-	-	-	10.4	-	-
DAP 1	0.6	0.8	1.0	1.2	1.1	0.8	0.5	1.4

	I	II	III	IV	V	VI	VII	VIII
Nonionic	1.5	2.0	2.0	2.2	1.0	4.2	4.0	6.5
PAAC	-	-	0.02	0.009	-	-	-	-
MnTACN	-	-	-	-	0.007	-	-	-
TAED	2.7	2.4	-	-	-	2.1	0.7	1.6
HEDP	1.0	-	-	0.9	-	0.4	0.2	-
DETPMP	0.7	-	-	-	-	-	-	-
Paraffin	0.4	0.5	0.5	0.5	-	-	0.5	-
BTA	0.2	0.3	0.3	0.3	0.3	0.3	0.3	-
Polycarboxylate	4.0	-	-	-	4.9	0.6	0.8	-
PEG	-	-	-	-	-	2.0	-	2.0
Glycerol	-	-	-	-	-	0.4	-	0.5
Perfume	-	-	-	0.05	0.2	0.2	0.2	0.2
Weight of tablet	20g	25g	20g	30g	18g	20g	25g	24g
pH	10.7	10.6	10.7	10.7	10.9	11.2	11.0	10.8
Miscellaneous, sulfate and water	Up to 100%							

### Example 23

- 5 The following compact high density (0.96Kg/l) dishwashing detergent compositions were prepared according to the present invention :

	I	II	III	IV	V	VI
STPP	-	51.0	51.0	-	-	44.3
Citrate	17.0	-	-	50.0	40.2	-
Carbonate	17.5	14.0	20.0	-	8.0	33.6
Bicarbonate	-	-	-	26.0	-	-
Silicate	15.0	15.0	8.0	-	25.0	3.6
Metasilicate	2.5	4.5	4.5	-	-	-
Catalyst	0.01	0.005	0.1	2.0	0.01	0.005
PB1	10.0	8.0	8.0	-	-	-
PB4	-	-	-	10.0	-	-
Percarbonate	-	-	-	-	11.8	4.8
Nonionic	2.0	1.5	1.5	3.0	1.9	5.9
TAED	2.0	-	-	4.0	-	1.4
HEDP	1.0	-	-	-	-	-



	I	II	III	IV	V	VI
DETPMP	0.6	-	-	-	-	-
PAAC	-	0.01	0.01	-	-	-
Paraffin	0.5	0.4	0.4	0.6	-	-
Pectate lyase	0.04	0.001	0.03	0.005	0.005	0.005
Protease	0.072	0.053	0.053	0.026	0.059	0.01
Amylase	0.012	0.012	0.012	0.021	0.021	0.006
Lipase	-	0.001	-	0.005	-	-
BTA	0.3	0.2	0.2	0.3	0.3	0.3
Polycarboxylate	6.0	-	-	-	4.0	0.9
Perfume	0.2	0.1	0.1	0.2	0.2	0.2
pH	11.0	11.0	11.3	9.6	10.8	10.9
Miscellaneous, sulfate and water	Up to 100%					

Example 24

- 5 The following granular dishwashing detergent compositions of bulk density 1.02Kg/L were prepared according to the present invention :

	I	II	III	IV	V	VI
STPP	30.0	33.5	27.9	29.6	33.8	22.0
Carbonate	30.5	30.5	30.5	23.0	34.5	45.0
Silicate	7.0	7.5	12.6	13.3	3.2	6.2
Metasilicate	-	4.5	-	-	-	-
Catalyst	0.01	0.2	0.005	0.1	1.00	0.5
Percarbonate	-	-	-	-	4.0	-
PB1	4.4	4.5	4.3	-	-	-
NADCC	-	-	-	2.0	-	0.9
Nonionic	1.0	0.7	1.0	1.9	0.7	0.5
TAED	1.0	-	-	-	0.9	-
PAAC	-	0.004	-	-	-	-
Paraffin	0.25	0.25	-	-	-	-
Pectate lyase	0.004	0.005	0.001	0.02	0.02	0.001
Protease	0.036	0.021	0.03	-	0.006	-
Amylase	0.03	0.005	0.004	-	0.005	-
Lipase	0.005	-	0.001	-	-	-

	I	II	III	IV	V	VI
BTA	0.15	0.15	-	-	0.2	-
Perfume	0.2	0.2	0.05	0.1	0.2	-
pH	10.8	11.3	11.0	10.7	11.5	10.9
Miscellaneous, sulfate and water	Up to 100%					

### Example 25

- 5 The following tablet detergent compositions were prepared according to the present invention by compression of a granular dishwashing detergent composition at a pressure of 13KN/cm<sup>2</sup> using a standard 12 head rotary press:

	I	II	III	IV	V	VI	VII	VIII
STPP	-	48.8	54.7	38.2	-	52.4	56.1	36.0
Citrate	20.0	-	-	-	35.9	-	-	-
Carbonate	20.0	5.0	14.0	15.4	8.0	23.0	20.0	28.0
Silicate	15.0	14.8	15.0	12.6	23.4	2.9	4.3	4.2
Pectate lyase	0.001	0.001	0.01	0.004	0.02	0.02	0.001	0.005
Protease	0.042	0.072	0.042	0.031	0.052	0.023	0.023	0.029
Amylase	0.012	0.012	0.012	0.007	0.015	0.003	0.017	0.002
Lipase	0.005	-	-	-	-	-	-	-
Catalyst	0.001	0.003	0.05	0.001	0.001	0.003	0.01	0.001
PB1	14.3	7.8	11.7	12.2	-	-	6.7	8.5
PB4	-	-	-	-	22.8	-	3.4	-
Percarbonate	-	-	-	-	-	10.4	-	-
Nonionic	1.5	2.0	2.0	2.2	1.0	4.2	4.0	6.5
PAAC	-	-	0.02	0.009	-	-	-	-
TAED	2.7	2.4	-	-	-	2.1	0.7	1.6
HEDP	1.0	-	-	0.9	-	0.4	0.2	-
DETPMP	0.7	-	-	-	-	-	-	-
Paraffin	0.4	0.5	0.5	0.5	-	-	0.5	-
BTA	0.2	0.3	0.3	0.3	0.3	0.3	0.3	-
Polycarboxylate	4.0	-	-	-	4.9	0.6	0.8	-
PEG	-	-	-	-	-	2.0	-	2.0
Glycerol	-	-	-	-	-	0.4	-	0.5
Perfume	-	-	-	0.05	0.2	0.2	0.2	0.2

	I	II	III	IV	V	VI	VII	VIII
Weight of tablet	20g	25g	20g	30g	18g	20g	25g	24g
pH	10.7	10.6	10.7	10.7	10.9	11.2	11.0	10.8
Miscellaneous, sulfate and water						Up to 100%		

Example 26

The following liquid rinse aid compositions were prepared according to the present invention :

	I	II	III	IV
Pectate lyase	0.001	0.0005	0.01	0.001
Pectin lyase	0.001	0.001	-	0.001
Catalyst	0.1	0.01	0.008	0.001
Nonionic	10.0	13.6	62.3	60.0
Propylene glycol	-	-	5.0	5.5
Citric	3.5	4.6	-	-
SCS	10.0	7.7	-	-
pH of the liquid	3.0	2.5	7.2	7.2
5 Miscellaneous, solvent and water	Up to 100%			

Example 27

10 The following automatic dishwashing tablets were made in accordance with the present invention (g of raw material and enzymes are expressed in pure enzyme) :

	I	II	III	IV	V	VI
<u>Phase 1</u>						
STPP	9.6	9.6	10.6	9.6	9.6	10.6
Silicate	0.5	0.7	2.9	0.5	0.7	2.9
SKS-6	1.5	1.5	-	1.5	1.5	-
Carbonate	2.3	2.7	2.8	2.3	2.7	2.8
HEDP	0.2	0.2	0.2	0.2	0.2	0.2
PB1	2.4	2.4	2.8	2.4	2.4	2.8
PAAC	0.002	0.002	-	-	-	-
Catalyst	-	-	-	0.002	0.002	-
BB1	0.2	0.5	-	-	-	-
DAP 1	-	-	0.5	-	-	0.2
Amylase	0.1	0.1	0.001	0.1	0.1	0.001
Protease	0.06	0.06	0.002	0.06	0.06	0.002
Nonionic	0.4	0.8	0.4	0.4	0.8	0.4

	I	II	III	IV	V	VI
PEG 6000	0.4	0.26	-	0.4	0.26	-
BTA	0.04	0.04	0.06	0.04	0.04	0.06
Paraffin	0.1	0.10	0.1	0.1	0.10	0.1
Perfume	0.02	0.02	0.02	0.02	0.02	0.02
<u>Total</u>	17.7g	18.5g	20.1g	17.7g	18.5g	20.1g
<u>Phase 2</u>						
Pectate Lyase	0.005	0.5	0.2	0.005	0.5	0.2
Pectin lyase	0.001	-	-	0.001	-	-
Amylase	0.003	0.003	0.004	0.003	0.003	0.004
Protease	0.01	0.009	0.01	0.01	0.009	0.01
Citric acid	0.3	-	0.6	0.3	-	0.6
Sulphamic acid	-	0.3	-	-	0.3	-
Bicarbonate	1.1	0.4	0.6	1.1	0.4	0.6
Carbonate	-	0.5	-	-	0.5	-
Triacetin	-	-	1.2	-	-	1.2
CaCl <sub>2</sub>	-	0.07	0.1	-	0.07	0.1
PEG 6000	-	-	1.2	-	-	1.2
PEG 3000	0.06	0.06	-	0.06	0.06	-
<u>Total</u>	2.05g	2.50g	23.6g	2.05g	2.50g	23.6g

- The tablet compositions I and II are prepared as follows. The detergent active composition of phase 1 is prepared by admixing the granular and liquid components and is then passed into the die of a conventional rotary press. The press includes a punch suitably shaped for forming a mould. The cross-section of the die is approximately 30x38 mm. The composition is then subjected to a compression force of 940 kg/cm<sup>2</sup> and the punch is then elevated exposing the first phase of the tablet containing the mould in its upper surface. The detergent active composition of phase 2 is prepared in similar manner and is passed into the die. The particulate active composition is then subjected to a compression force of 170 kg/cm<sup>2</sup>, the punch is elevated, and the multi-phase tablet ejected from the tablet press. The resulting tablets dissolve or disintegrate in a washing machine as described above within 12 minutes, phase 2 of the tablets dissolving within 5 minutes. The tablets display improved strength, especially on long-term storage, together with excellent dissolution characteristics.

The tablet composition III was prepared as follows : The compressed portion is prepared by delivering the composition of active detergent components to a punch cavity of a modified rotary tablet press and compressing the composition at a pressure of 940kg/cm<sup>2</sup>. The modified tablet press provides tablet wherein

5 the compressed portion has a mould. For the purposes of Example III, the non-compressed portion is in particulate form. The non-compressed portion is accurately delivered to the mould of the compressed portion using a nozzle feeder. The non-compressed portion is adhered to the compressed portion by

10 coating the non-compressed portion with a coating layer which contacts the compressed portion.

## WHAT IS CLAIMED IS:

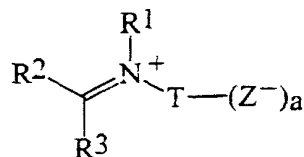
1. A detergent composition comprising a detergent ingredient, a pectate lyase enzyme and bleach system selected from the group consisting of a metal bleach catalyst; a combination of a peroxygen source and a bleach booster selected from the group consisting of zwitterionic imines, anionic imine polyions having a net negative charge of from -1 to -3, and/or mixtures thereof; a diacyl peroxide and/or mixtures thereof.
2. A detergent composition according to claim 1 wherein the metal bleach catalyst is selected from :
  - (a) the  $[Mn(Bcyclam)Cl_2]$  catalyst;
  - (b) the cobalt catalyst having the formula :  $Co[(NH_3)_n M_m B_b T_t Q_q P_p] Y_y$  wherein Cobalt is in the +3 oxidation from, n is an integer from 0 to 5, preferably 4-5, more preferably 5; M represents a monodentate ligand; m is an integer from 0-5, preferably 1 or 2, more preferably 1; B represents a bidentate ligand; b is an integer from 0-2; T represents a tridentate ligand; t is 0 or 1; Q is a tetradentate ligand; q is 0 or 1; P is an pentadentate ligand; p is 0 or 1 and  $n+m+2b+3t+4q+5p=6$ ; Y is one or more appropriately selected counteranions present in a number y, where y is an integer from 1-3, preferably 2-3, more preferably 2 when Y is a -1 charged anion, to obtain a charge-balanced salt;
  - (c) the cobalt catalyst having the formula  $[Co(NH_3)_5 M] T_y$  wherein cobalt is in the +3 oxidation state; M is a carboxylate-containing ligand having the formula  $RC(O)O^-$ ; and T is one or more counteranions present in a number y, where y is an integer to obtain a charge-balanced salt (preferably from 1-3, more preferably 2 when T is a -1 charged anion); and/or mixtures thereof.
3. A detergent composition according to 1-2 comprising said metal bleach catalyst and further comprising a peroxygen source, preferably selected from the group consisting of a hydrogen peroxide source, a peroxyacid bleach precursor compound, and/or mixtures thereof.

4. A composition according to claims 2-3 wherein the metal bleach catalyst is present in an amount of from 1ppb to 10%, preferably from 0.1ppm to 1%, more preferably from 1ppm to 0.1% by weight of total composition.
5. A detergent composition according to any of the preceding claims wherein said diacyl peroxide is selected from the group consisting of dibenzoyl peroxide, benzoyl glutaryl peroxide, benzoyl succinyl peroxide, di(2-methyl benzoyl) peroxide, and/or mixtures thereof.
6. A detergent composition according to claim 5 wherein said diacyl peroxide is dibenzoyl peroxide.
7. A detergent composition according to any of the preceding claims wherein said diacyl peroxide is comprised in a particle; said particle comprising from 1-80% by weight of said particle of diacyl peroxide, from 0.01-95% by weight of said particle of a water soluble stabilising additive.
8. A detergent composition according to claim 7 wherein said stabilising additive is selected from the group consisting of alkali metal sulfates and citrates, ethoxylated C16-20 alcohols, polyethylene glycols melting above 100°F, maltodextrins, polyacrylate polymers and copolymers of molecular weight between 1.000 and 80.000, ethylene diamine tetra-acetates, ethylene diamine disuccinates and/or mixtures thereof.
9. A detergent composition according to claim 1-4 wherein said diacyl peroxide is dilauroyl peroxide.
10. A detergent composition according to any of the preceding claims wherein said diacyl peroxide is comprised at a level of from 0.01% to 20% by weight of the composition, preferably 0.5% to 10%, more preferably 0.2% to 3%.
11. A detergent composition according to claims 7-10 wherein the diacyl peroxide is incorporated into a particulate and said particle is comprised at a level of from 0.1% to 30%, preferably from 1% to 15%, more preferably from 1.5% to 10% of the total composition.

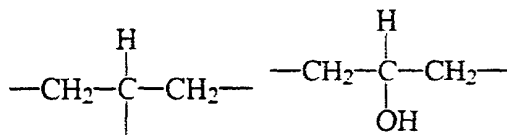


12. A detergent composition according to any of the preceding claims wherein said bleach booster is selected from the group consisting of aryliminium zwitterions, aryliminium polyions having a net negative charge of from -1 to -3; and/or mixtures thereof.

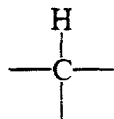
13. A detergent composition according to claim 12 wherein said bleach booster has the formula:



wherein R<sup>1</sup>-R<sup>3</sup> are moieties having a total charge of from about 0 to about -1; R<sup>1</sup> and R<sup>2</sup> form part of a common ring; T is selected from the group consisting of: -(CH<sub>2</sub>)<sub>b</sub>- wherein b is from about 1 to about 8, -(CH(R<sup>5</sup>))- wherein R<sup>5</sup> is C<sub>1</sub>-C<sub>8</sub> alkyl, -CH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)-,

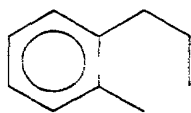


and -(CH<sub>2</sub>)<sub>d</sub>(E)(CH<sub>2</sub>)<sub>f</sub>- wherein d is from 2 to 8, f is from 1 to 3 and E is -C(O)O-, -C(O)NR<sup>6</sup> or :



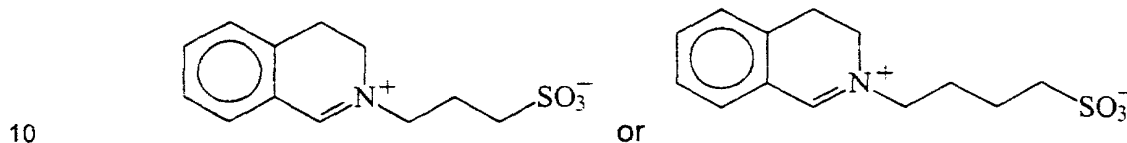
- wherein R<sup>6</sup> is H or C<sub>1</sub>-C<sub>4</sub> alkyl; Z is covalently bonded to T and Z is selected from the group consisting of -CO<sub>2</sub><sup>-</sup>, -SO<sub>3</sub><sup>-</sup> and -OSO<sub>3</sub><sup>-</sup> and a is either 1 or 2.

14. A detergent composition according to claims 12-13 wherein R<sup>1</sup> and R<sup>2</sup> together form the non-charged moiety:

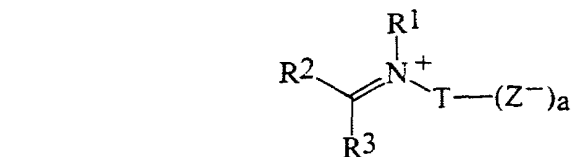


15. A detergent composition according to claims 12-14 wherein said bleach booster is an aryliminium zwitterion and  $R^3$  is H, T is  $-(CH_2)_b-$  or  $-CH_2(C_6H_4)-$ , Z is  $-SO_3^-$ , a is 1 and b is from 2 to 4.

16. A detergent composition according to claims 12-15 wherein said bleach booster is an aryliminium zwitterion having the formula:

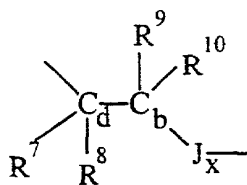


17. A detergent composition according to claim 12 wherein said bleach booster has the following formula:



wherein  $R^1 - R^3$  is hydrogen or an unsubstituted or substituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl and cycloalkyl radicals;  $R^1$  and  $R^2$  form part of a common ring; T has the

20 formula:

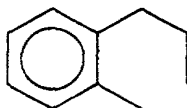


wherein x is equal to 0 or 1; J, when present, is selected from the group consisting of  $-CR^{11}R^{12}-$ ,  $-CR^{11}R^{12}CR^{13}R^{14}-$ , and  $-CR^{11}R^{12}CR^{13}R^{14}CR^{15}R^{16}-$ ;  $R^7-R^{16}$  are selected from the group

25 consisting of H, linear or branched  $C_1-C_{18}$  substituted or unsubstituted

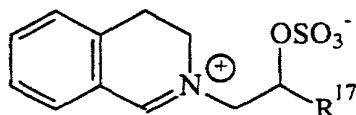
alkyl, alkylene, oxyalkylene, aryl, substituted aryl, substituted arylcarbonyl groups, and amide groups; provided that at least one of  $R^7$ - $R^8$  must be H or methyl, and that when neither  $R^9$  nor  $R^{10}$  is H, one of  $R^7$ - $R^8$  must be H; Z is covalently bonded to  $J_x$  when x is 1 and to  $C_b$  when x is 0; and Z is selected from the group consisting of  $-CO_2^-$ ,  $-SO_3^-$  and  $-OSO_3^-$ , and a is 1.

18. A detergent composition according to claim 17 wherein said bleach booster wherein  $R_1$  and  $R_2$  are defined in its formula as  $R_1$  and  $R_2$  together form the non-charged moiety:



19. A detergent composition according to claims 17-18 wherein said bleach booster is an aryliminium zwitterion and  $R^3$  is H, Z is  $-OSO_3^-$ , a is 1.

20. A detergent composition according to claims 17-19 wherein said bleach booster is an aryliminium zwitterion having the formula:



- where  $R^{17}$  is selected from the group consisting of H and linear or branched  $C_1$ - $C_{18}$  substituted or unsubstituted alkyl.

21. A detergent composition according to any of the preceding claims wherein said bleach booster is comprised at a level of from 0.01% to 10% by weight of the total composition.

22. A detergent composition according to claims 12-21 wherein said peroxygen source is comprised at a level of from 0.01% to 60% by weight of the total composition.

23. A detergent composition according to claims 12-22 wherein said peroxygen source comprises a preformed peracid compound selected from the group

consisting of percarboxylic acids and salts, percarbonic acids and salts, perimidic acids and salts, peroxymonosulfuric acids and salts, and/or mixtures thereof; a hydrogen peroxide source, a bleach activator and/or mixtures thereof.

- 5
24. A detergent composition according to claim 23 wherein said hydrogen peroxide source is selected from the group consisting of perborate compounds, percarbonate compounds, perphosphate compounds and/or mixtures thereof.
- 10
25. A detergent composition according to claim 23 wherein said bleach activator is selected from the group consisting of tetraacetylenediamine, sodium decanoyloxybenzene sulfonate, sodium nonanoyloxybenzene sulfonate, sodium octanoyloxybenzene sulfonate, (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamido-caproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and/or mixtures thereof.
- 15
26. A detergent composition according to any of the preceding claims wherein said pectate lyase is present at a level of from 0.0001% to 2%, preferably from 0.0005% to 1.0, more preferably from 0.001% to 0.5% pure enzyme by weight of total composition.
- 20
27. A detergent composition according to any of the preceding claims further comprising a pectin lyase.
- 25
28. Use of a composition according to any of the preceding claims for the removal of plant-, dirt-based stains, highly coloured food soils/stains and body soils.
- 30
29. Use of a composition according to any of the preceding claims for superior fabric whiteness maintenance.
- 35
30. Use of a composition according to claims 5-11 for effective highly coloured stains and soils removal on plasticware, and/or for preventing the staining and/or discolouration of the dishware by highly coloured components.

	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100	2101	2102	2103	2104	2105	2106	2107	2108	2109	2110	2111	2112	2113	2114	2115	2116	2117	2118	2119	2120	2121	2122	2123	2124	2125	2126	2127	2128	2129	2130	2131	2132	2133	2134	2135	2136	2137	2138	2139	2140	2141	2142	2143	2144	2145	2146	2147	2148	2149	2150	2151	2152	2153	2154	2155	2156	2157	2158	2159	2160	2161	2162	2163	2164	2165	2166	2167	2168	2169	2170	2171	2172	2173	2174	2175	2176	2177	2178	2179	2180	2181	2182	2183	2184	2185	2186	2187	2188	2189	2190	2191	2192	2193	2194	2195	2196	2197	2198	2199	2200	2201	2202	2203	2204	2205	2206	2207	2208	2209	2210	2211	2212	2213	2214	2215	2216	2217	2218	2219	2220	2221	2222	2223	2224	2225	2226	2227	2228	2229	2230	2231	2232	2233	2234	2235	2236	2237	2238	2239	2240	2241	2242	2243	2244	2245	2246	2247	2248	2249	2250	2251	2252	2253	2254	2255	2256	2257	2258	2259	2260	2261	2262	2263	2264	2265	2266	2267	2268	2269	2270	2271	2272	2273	2274	2275	2276	2277	2278	2279	2280	2281	2282	2283	2284	2285	2286	2287	2288	2289	2290	2291	2292	2293	2294	2295	2296	2297	2298	2299	2300	2301	2302	2303	2304	2305	2306	2307	2308	2309	2310	2311	2312	2313	2314	2315	2316	2317	2318	2319	2320	2321	2322	2323	2324	2325	2326	2327	2328	2329	2330	2331	2332	2333	2334	2335	2336	2337	2338	2339	2340	2341	2342	2343	2344	2345	2346	2347	2348	2349	2350	2351	2352	2353	2354	2355	2356	2357	2358	2359	2360	2361	2362	2363	2364	2365	2366	2367	2368	2369	2370	2371	2372	2373	2374	2375	2376	2377	2378	2379	2380	2381	2382	2383	2384	2385	2386	2387	2388	2389	2390	2391	2392	2393	2394	2395	2396	2397	2398	2399	2400	2401	2402	2403	2404	2405	2406	2407	2408	2409	2410	2411	2412	2413	2414	2415	2416	2417	2418	2419	2420	2421	2422	2423	2424	2425	2426	2427	2428	2429	2430	2431	2432	2
--	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	---

My residence, post office and citizenship are as stated below next to my name.

## "Detergent Compositons Comprising a Pectate Lyase and a Bleach System"

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims.

I hereby claim foreign priority benefits under Title 35 United States Code §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

PCT/US99/00800	PCT	14 January 1999
PCT/US99/00803	PCT	14 January 1999
PCT/US99/00790	PCT	14 January 1999
PCT/US99/00801	PCT	14 January 1999
PCT/US99/00802	PCT	14 January 1999

I hereby claim the benefit under Title 35 United States Code §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35 United States Code §112, I acknowledge the duty to disclose material information as defined in Title 37 Code of Federal Regulations §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Appln. Serial No.	Filing Date	Status - patented, pending, abandoned
Appln. Serial No.	Filing Date	Status - patented, pending, abandoned

I hereby appoint the following as my attorney(s) or agent(s) with full power of substitution to prosecute this application and transact all business in the Patent and Trademark office connected therewith:

Name	Registration No.	Associate Power of Attorney Attached [ ] Yes [ ] No
Jacobus C. Rasser	<u>37,043</u>	
T. David Reed	<u>32,931</u>	
Eileen L. Hughett	<u>34,352</u>	
Timothy B. Guffey	<u>41,048</u>	
Emelyn L. Hiland	<u>41,501</u>	

SEND CORRESPONDENCE TO:

T. David Reed, c/o The Procter Gamble Company (513) 627-7025  
Name Phone No.  
5299 Spring Grove Avenue Cincinnati Ohio 45217-1087  
Street City State Zip Code

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-00  
Full name of sole or first inventor: SHOWELL, Michael Stanford  
Inventor's signature Michael Stanford Showell Date 11-02-2001  
Residence: 685 Compton Road Cincinnati, Ohio 45231 US OH  
Citizenship: US  
Post Office Address: 5299 Spring Grove Ave., Cincinnati, Ohio 45217-1087

2-00  
Full name of second joint inventor, if any: ZHU, Yong  
Inventor's signature Yong Zhu Date 10-30-2001  
Residence: 4348 Bromyard Avenue Cincinnati, Ohio 45241 US OH  
Citizenship: ~~CA~~ US  
Post Office Address: 5299 Spring Grove Ave., Cincinnati, Ohio 45217-1087

3-00  
Full name of third joint inventor, if any: MOESE, Rosa Laura  
Inventor's signature R. Laura Moese Date 10-30-2001  
Residence: 8815 Eagle Creek Court West Chester, Ohio 45069 US OH  
Citizenship: US  
Post Office Address: 5299 Spring Grove Ave., Cincinnati, Ohio 45217-1087

4-00  
Full name of fourth joint inventor, if any: BETTIOL, Jean-Luc Philippe  
Inventor's signature J. Bettiol Date 11.11.01  
Residence: 93 Avenue Slegers B-1200 Brussels BE BEX  
Citizenship: FR  
Post Office Address: 5299 Spring Grove Ave., Cincinnati, Ohio 45217-1087

5-00  
Full name of fifth joint inventor, if any: BUSCH, Alfred  
Inventor's signature *Alfred Busch* Date Ver. 15-01  
Residence: Handelsstraat 210 B-1840 Londerzeel BE  
Citizenship: DE  
Post Office Address: 5299 Spring Grove Ave., Cincinnati, Ohio 45217-1087  
BEX

6-00  
Full name of sixth joint inventor, if any: WELLS, Eric C.  
Inventor's signature *Eric Wells* Date 10/31/01  
Residence: 1440 W. Kemper Road, #1601, Cincinnati, Ohio 45240  
Citizenship: US  
Post Office Address: 5299 Spring Grove Ave., Cincinnati, Ohio 45217-1087  
OH

TOPT-666666

CM2000XM

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the U.S. National Phase Entry  
Under 35 USC 371 from  
International Application of  
SHOWELL, Michael Stanford et al.  
Int'l. Application No. PCT/US00/00838  
Filed in the RO/US on 13 January 2000  
Entitled: *Detergent Compositions Comprising A  
Pectate Lyas and A Bleach System*

ASSOCIATE POWER OF ATTORNEY

Assistant Commissioner for Patents  
Box PCT  
Washington, D.C. 20231

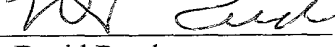
Dear Sir:

You are requested to recognize K. W. Zerby (Registration No. 32,323), B. M. Bolam (Registration No. 37,513), F. C. Turner (Registration No. 39,863), C. B. Cook (Registration No. 39,151), M. Dressman (Registration No. 42,498), and R. S. Echler, Sr. (Registration No. 41,006) of The Procter & Gamble Company, Cincinnati, Ohio, as Associate Attorneys to prosecute this application, to make alterations and amendments therein, and to transact all business in the Patent Office connected with the application or with the patent granted thereupon.

Please address all future communications to:

F. Taffy  
Customer Number 27748

Respectfully submitted for Applicants,

By   
T. David Reed  
Agent for Applicant  
Registration No. 32,931

Cincinnati, Ohio  
13 July 2001  
(513) 627-7025/FAX 627-6333

FOIA b 6, b 7C, b 7D